**♻EPA**

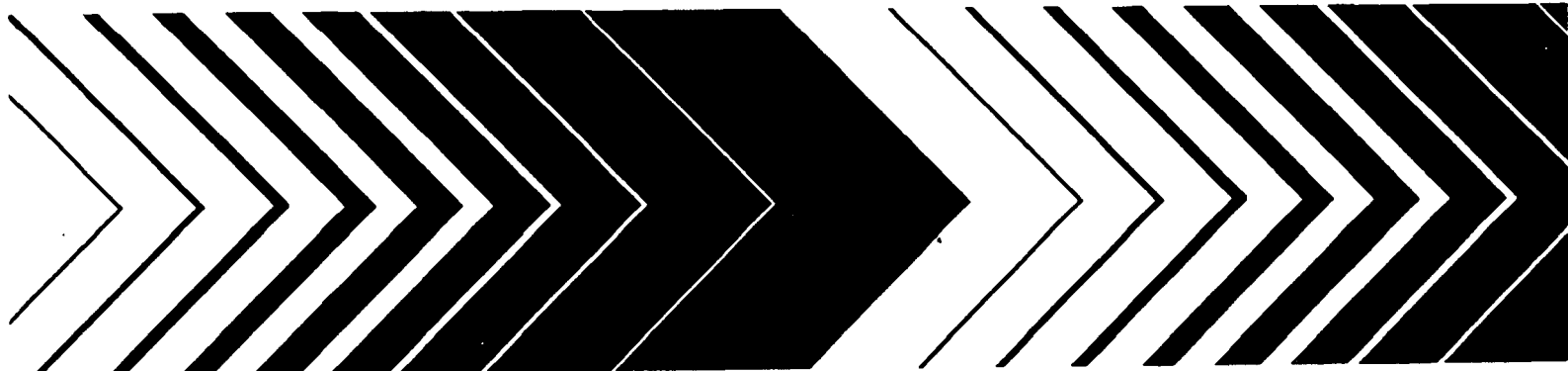# Automated On-Site Measurement of Volatile Organic Compounds in Water

# A Demonstration of the A⁺RT, Inc. Volatile Organic Analysis System

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# NOTICE

# Abstract

A demonstration of the performance of the Analytic and Remedial Technology, Inc. Volatile Organic Analysis System (AVOAS) is described. The AVOAS is designed to provide automated collection and analysis of water samples containing volatile organic compounds (VOCs). In this demonstration, the AVOAS was used to monitor VOCs at a pilot pump-and-treat ground-water remediation facility. The demonstration was conducted by the U.S. Environmental Protection Agency (EPA) through the Superfund Innovative Technology Evaluation (SITE) Program at a Superfund site in Woburn, Massachusetts in May, 1991.

The AVOAS consists of a manifold which permits sampling from multiple locations; an injector which extracts the VOCs from aqueous samples by a proprietary process similar to purge and trap and injects them into a gas chromatograph; and software that provides system control and storage of data. The proposed advantages of the AVOAS are that it eliminates the steps typically associated with collection and analysis of water samples and provides real-time results.

The demonstration was performed at a site where the ground water is contaminated with volatile chlorinated hydrocarbons. The performance of the AVOAS was compared with that of an established method (EPA Method 502.2). In addition to on-line monitoring of the ground-water treatment system, samples spiked with measured concentrations of analytes were processed for purposes of evaluation and quality control. The demonstration was designed to detect sources of variability between the field and conventional laboratory techniques. On the basis of results from this short-term study, we conclude that the AVOAS is capable of providing the benefits of automated sampling and analysis, as proposed. AVOAS recoveries for samples spiked with known concentrations of VOCs were higher than those of Method 502.2, and were close to 100% for most analytes. Precision was within limits acceptable for VOC analyses (within 30 percent relative standard deviation). Further development of the AVOAS is encouraged, and a longer term evaluation at other sites is recommended.

This evaluation report is submitted by Lockheed Engineering & Sciences Company in partial fulfillment of Contract Number 68-C0-0049 with the U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

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# List of Abbreviations and Acronyms

| | |
|---|---|
| 1,1-DCA | 1,1-dichloroethane |
| 1,1-DCE | 1,1-dichloroethene |
| 1,1,1-TCA | 1,1,1,-trichloroethane |
| 1,2-DCA | 1,2-dichloroethane |
| A$^+$RT | Analytic and Remedial Technology, Inc. |
| AFMMP | Advanced Field Monitoring Methods Program |
| ANOVA | Analysis of variance |
| AVOAS | A$^+$RT Volatile Organic Analysis System |
| CCCS | continuing calibration check standard |
| cis-1,2-DCE | cis-1,2-dichloroethene |
| CLP | Contract Laboratory Program |
| DQO | data quality objective |
| ELCD | electrolytic conductivity detector |
| EMSL-LV | Environmental Monitoring Systems Laboratory-Las Vegas |
| EPA | Environmental Protection Agency |
| EPC | Environmental Project Control, Inc. |
| GC | gas chromatograph |
| HCl | hydrochloric acid |
| LESC | Lockheed Engineering & Sciences Company |
| MDL | method detection limit |
| Method 502.2 | EPA Method 502.2, "Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series" |
| %D | percent difference |
| %R | percent recovery |
| PCE | tetrachloroethene (perchloroethene) |
| PEW | purged effluent water |
| PE | performance evaluation |
| PID | photoionization detector |
| ppb | parts per billion |
| ppm | parts per million |
| PQL | practical quantitation limit |
| QA | quality assurance |
| QAPjP | Quality Assurance Project Plan |
| QC | quality control |
| QCCS | quality control check standard |
| RSD | relative standard deviation |
| RT | retention time |
| SARA | Superfund Amendments and Reauthorization Act |

## List of Abbreviations and Acronyms (continued)

| | |
|---|---|
| SITE | Superfund Innovative Technology Evaluation |
| SPEW | spiked purged effluent water |
| TCE | trichloroethene |
| trans-1,2-DCE | trans-1,2-dichloroethene |
| TT | treatment train |
| UV | ultraviolet |
| VC | vinyl chloride |
| VOA | volatile organic analysis |
| VOC | volatile organic compound |

# Acknowledgments

# Executive Summary

An automated system designed to monitor volatile organic compounds (VOCs) in a water-treatment process stream was evaluated under the U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) Program. The monitoring system evaluated was the Analytic and Remedial Technology, Inc., Volatile Organic Analysis System (AVOAS). The AVOAS permits unattended sampling from multiple locations, with extraction of VOCs from the samples by a proprietary process similar to purge and trap, and analysis by gas chromatography (GC).

The demonstration was conducted under the guidance of the EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV), as part of the Monitoring and Measurement Technologies portion of the SITE Program. A mandate of the SITE Program is to identify cost-effective alternatives to existing methods used in characterizing and remediating contamination at Superfund sites. SITE demonstrations provide a mechanism for evaluating selected technologies that are at least comparable in quality and cost to established methods.

Currently, most methods for processing samples used to monitor remediation at Superfund sites require a number of steps. These include sample collection, preservation, transport, storage, and analysis at off-site laboratories. The principal drawbacks to these procedures are the need for trained sampling personnel, the turnaround time for results, the cost per analysis, and, particularly for VOCs, the potential for changes in sample integrity between the time of sample collection and analysis. The proposed advantages of the AVOAS are that it replaces conventional sampling and analysis procedures and provides results within less than an hour of sampling (i.e., nearly real-time results). Further, the AVOAS continuously monitors the function of the various components of a treatment system, permitting process control capability. Malfunctions in a treatment system can be quickly detected as increased concentrations of VOCs, signalling the need for maintenance or other measures to correct the problem.

For the application evaluated in this demonstration, the AVOAS was incorporated as a dedicated component of a treatment system being tested at an EPA Region I Superfund site for remediating ground water contaminated with chlorinated VOCs. The treatment system was a series of discrete units designed to progressively reduce contaminant concentrations. The AVOAS measured VOC concentrations after each treatment unit.

The demonstration compared the performance of the AVOAS with that of EPA Method 502.2. The field portion of the demonstration was conducted May 18 through 24, 1991, at the Wells G and H Superfund Site in Woburn, MA. For the demonstration, the ground-water treatment system was operational, and samples were collected and analyzed in the monitoring mode for which the AVOAS was designed. Samples were also collected using standard methods for VOCs in water, and were analyzed by the AVOAS operated in the "off-line" mode and by Method 502.2 at the EMSL laboratory in Las Vegas, NV. In addition to samples from the treatment system, samples spiked with measured concentrations of analytes and a variety of quality assurance and quality control (QA/QC) samples were analyzed by each method.

A total of 96 samples analyzed by the AVOAS and the EMSL-LV instrument during the demonstration were used to assess the performance of the AVOAS. The AVOAS ran an average of 22.3 hours per day, which included approximately 8 hours per day of unattended operation. Only minor breakdowns occurred, and recalibration and maintenance requirements were minimal. The qualitative and quantitative findings generated in this demonstration provided the basis for the following observations about the performance of the AVOAS:

1) Concentration values generated by the AVOAS for virtually all samples were higher than those measured by Method 502.2; however, AVOAS analyte recovery values were closer to 100%. The cause of this finding cannot be resolved from the data available from this short-term study. The precision obtained by the AVOAS was comparable to that obtained by Method 502.2, and was within the expected range.

2) The AVOAS performed well in analyzing samples with VOC concentrations in the low-ppb to low-ppm range.

3) The proprietary system used by the AVOAS for stripping VOCs from water is simple in design and function and more adaptable to field automation than the traditional purge-and-trap procedure.

4) The demonstration showed that the AVOAS is capable of providing the benefits of automated sampling and analysis, as proposed. That is, it provides real-time results and eliminates manual sample collection, handling, shipping, and analysis steps as well as the potential for losses in sample integrity. In addition, the potential cost savings for use of the AVOAS in comparison to use of established methods could be substantial, particularly for processing large numbers of samples (i.e., for long-term, continuous monitoring).

The following items were identified as potential limitations to the use of the AVOAS. Many of these are not so much limitations, as factors that must be kept in mind or planned for by prospective users of the AVOAS. The AVOAS developer recognized some of these limitations during the demonstration, and has since taken steps to correct equipment or procedures.

1) The AVOAS requires a temperature-controlled environment and an atmosphere free of contamination. Although maintaining these conditions was not a problem at the location where this demonstration was conducted, extra measures to ensure these conditions may be required in other field situations or industrial facilities.

2) Water samples high in particulate matter tend to clog a filter in the injector inlet. The impact of this problem can be minimized if water is pre-filtered before being conveyed to the AVOAS. Also, cleaning and replacement of the filter can be incorporated as part of the routine maintenance procedures.

3) The possibility of carryover in the smallest sample loop of the AVOAS was suggested by the finding of an increase in trace concentrations of several analytes in ground-water treatment system (i.e., treatment train) samples between morning and afternoon analyses. The AVOAS developer has modified the design of the manifold to reduce dead volume significantly, and expects this change to greatly reduce the carryover problem.

4) Many of the (relatively minor) problems encountered with the AVOAS during the field demonstration were due to problems in the system software, most of which were corrected during the demonstration.

Based on the findings of this study, the following recommendations are made:

1) Further development of the AVOAS is encouraged, and additional studies should be performed. Performance data should be generated for this system when used at other sites, by different operators, and in the fully automated mode.

2) Instrument calibration should be checked regularly on a schedule based on the performance of the detector. A daily calibration check is recommended. If this is not feasible, at a minimum, detector performance should be monitored daily over a period of several weeks after instrument installation. An appropriate calibration schedule should be developed and followed for the long-term use of the system, especially for unattended, remote operation.

3) A mechanism for introducing surrogate standards into the AVOAS with each analysis would provide an ongoing indication of analytical instrument performance.

4) Depending on the data quality objectives for instrument performance at a particular site, blank samples should be periodically analyzed on all sampling loops, to ensure that carryover from high-concentration samples into low-concentration samples is not occurring.

5) During the initial stages of long-term monitoring, concentrations for each sampling port, as well as data on instrument precision should be closely monitored to generate expected baseline conditions. Periodic confirmatory analyses by established methods should be performed to verify instrument results.

# Section 1
# Introduction

The Analytic and Remedial Technology, Inc., Volatile Organic Analysis System (AVOAS) was evaluated under the U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) Program. The AVOAS is designed to monitor volatile organic compounds (VOCs) in water-treatment process streams. The system provides automated sampling from multiple locations, with extraction of VOCs from the samples by a proprietary process similar to purge and trap, and analysis by gas chromatography (GC). The purpose of the demonstration described in this report was to compare the performance of the AVOAS with that of an established method.

This section provides an overview of the SITE Program and descriptions of the AVOAS, the site of the demonstration, and the project organization. The rest of the report is organized into four sections. Section 2 describes the AVOAS demonstration; Section 3 presents and discusses the quantitative and qualitative results of the evaluation; and Section 4 presents the conclusions and recommendations based on the findings of the demonstration.

## SITE Program Background

The Superfund Program was initiated in 1980 to identify, prioritize, and remediate uncontrolled hazardous waste sites. Subsequently, the problems associated with hazardous waste sites proved to be far more complex than originally anticipated. In 1986, the U.S. Congress enacted the Superfund Amendments and Reauthorization Act (SARA), requiring the EPA to promote more effective hazardous waste site identification and cleanup. The SITE Program addresses Section 311(b) of SARA, which requires the EPA to establish "a program of research, evaluation, testing, development, and demonstration of alternative or innovative treatment technologies...which may be utilized in response actions to achieve more permanent pro-tection of human health and welfare and the environment."

Two categories of technologies are addressed under the SITE Program: (1) treatment technologies that may serve as alternatives to land disposal, and (2) technologies for measuring and monitoring contaminants at hazardous waste sites. This latter portion of the SITE Program is administered by the Advanced Field Monitoring Methods Program (AFMMP). The Environmental Monitoring Systems Laboratory at Las Vegas, Nevada (EMSL-LV) is the lead laboratory for the AFMMP, and provided oversight of the demonstration described in this report.

## AVOAS Technology Description

The AVOAS was designed by Gary Hopkins and Doug Mackay of Analytic and Remedial Technology, Inc. (A$^+$RT, Inc., Menlo Park, CA). The AVOAS consists of a sampling manifold and a purge-and-trap concentrator ("injector") connected to a gas chromatograph (GC). An integrator processes the GC signal data, and a computer is used to control the system and to store the data. The innovative components are the sampling manifold, the injector, and the computer software. The manifold permits on-line collection of samples from multiple locations. The injector collects a measured volume of water, strips the VOCs from the aqueous to the gas phase, traps them on a sorbent, and thermally desorbs them into the GC. The computer software handles data storage and controls the analytical system. With use of a modem, data can be transmitted off-site, allowing remote operation and control of the AVOAS, eliminating the need for the physical presence of the operator at the site. Figure 1-1 is a schematic of the AVOAS.

Among the features that can be controlled are the sampling sequence (i.e., the order in which the manifold valves are actuated); the flush time for
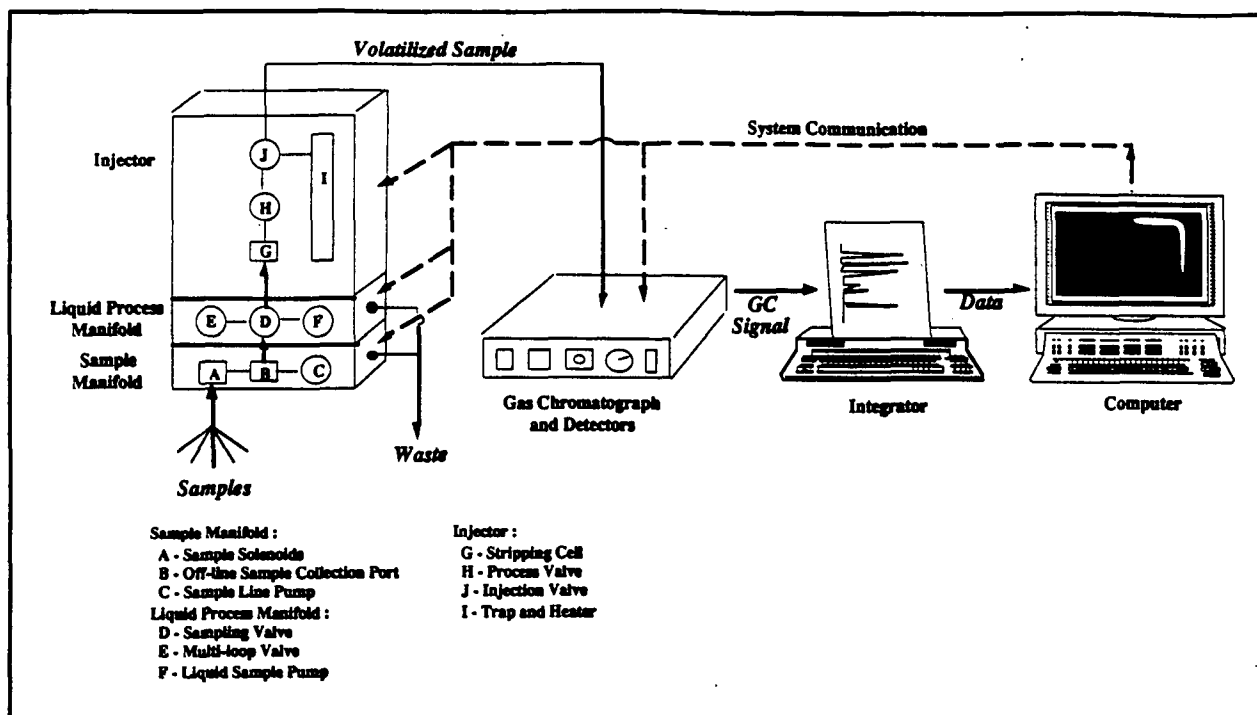
**Figure 1-1. Schematic of the AVOAS.**

the sampling lines; the sample size; and the integrator operating parameters. Sample size is controlled via a switching valve, which permits selection among sample loops of different internal volumes. To optimize detection of target analytes, the sample volume can be selected based on either prior knowledge of potential concentration ranges at a given sampling point or by computer logic. In the computer logic mode, the microcomputer is programmed to repeat a sample analysis using a different loop volume if the first measurement is out of the range of instrument detection or calibration. Sample sizes from 100 µL (the dead volume of the valve) to 10 mL or more are possible (the upper limiting volume is defined by the maximum sample processing time required for any application). The sampling loops are flushed with VOC-free water between samples. To minimize sample carryover (i.e., adsorption of compounds in samples to analytical surfaces they contact, followed by desorption into subsequent samples), the manifold and all sample loops and sample conveyance lines are constructed of stainless steel. External samples, including calibration standards and quality control (QC) samples, are introduced into the system through a line between the manifold and injector. Water samples from each sample port can be collected at the manifold for off-site, confirmatory laboratory analysis. The AVOAS can be used with virtually any GC and integrator, and can be

adapted to different purgeable analytes by selection of the appropriate GC column, temperature program, and detector. Earlier versions of the system have been used in site-specific research applications. The version evaluated in this demonstration had modifications intended to make the AVOAS a commercially marketable product.

For the application discussed in this report, the AVOAS functioned as a dedicated component of a treatment system being demonstrated at a Superfund site to remediate ground water contaminated with chlorinated VOCs. The treatment system consisted of a series of discrete units designed to provide a stepwise reduction in contaminant concentrations. The AVOAS measured VOC concentrations at selected locations in the groundwater treatment system.

## AVOAS Demonstration Overview

### Purpose of the AVOAS Demonstration

The purpose of this demonstration was to compare the performance of the AVOAS while operating at the site of a remediation with that of an established method conducted in a fixed-base laboratory. EPA Method 502.2, "Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in

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Series - Revision 2," was selected for comparison, because operation of the AVOAS most closely follows the specifications of that method. This SITE demonstration was not intended to evaluate the ground-water treatment system.

The primary goal of the demonstration was to generate data of sufficient quality, quantity, and type, by both the AVOAS and the comparison method, to permit a sound interpretation of results. A demonstration plan prepared prior to the AVOAS evaluation identified the specific study objectives and described in detail the sampling, analysis, and QA/QC activities required to meet those objectives.

Qualitative measures of system performance (ruggedness, reliability, maintenance requirements, facility and supply requirements, and cost) were not specifically defined in the AVOAS Demonstration Plan; however, these measures were informally evaluated and are discussed in this report. Performance characteristics such as specificity and interferences, which are determined by the detection system (i.e., the chromatographic column, gas chromatograph, and detector), were not considered in this demonstration because these characteristics are not a function of the innovative components of the AVOAS.

## Demonstration Site Description

The AVOAS demonstration was performed at the Wells G and H Superfund Site in Woburn, Massachusetts. The site covers 330 acres and includes the aquifer and land in the vicinity of two former municipal drinking water wells (Wells G and H). Figure 1-2 is an area map of the site.

Wells G and H had been used as a source of municipal water until, in 1979, the Massachusetts Department of Environmental Protection detected contamination by chlorinated VOCs in water samples from the wells. The primary contaminants include trichloroethene (TCE) and tetrachloroethene (PCE), with lesser amounts of 1,1-dichloroethene (1,1-DCE), cis-1,2-dichloroethene (cis-1,2-DCE), trans-1,2-dichloroethene (trans-1,2-DCE), 1,1-dichloroethane (1,1-DCA), and 1,1,1-trichloroethane (1,1,1-TCA). In December 1982, the EPA put the site on the National Priority List, and in September 1989, a Record of Decision was issued requiring that the ground water beneath the site be treated to remove the contamination.

A pilot demonstration (conducted under a different program) of a ground-water treatment system installed in the Unifirst Facility presented the opportunity to simultaneously evaluate the performance of the AVOAS. The treatment system pilot demonstration was May 18 through May 30, 1991, and the field portion of the AVOAS SITE demonstration was conducted over the 6-day period of May 18 through 24. During the pilot demonstration, the treatment process included units for ultraviolet/chemical oxidation, carbon adsorption, and reductive dehalogenation. Figure 1-3 is a schematic of the ground-water treatment system. Sampling ports at selected locations permitted monitoring the concentration of VOCs before and after each treatment step. The sampling ports used to evaluate the AVOAS included port S-3 (after the carbon drum, before the oxidation unit) and port S-4 (after the reductive dehalogenation unit, before the oxidation unit). Sample collection from two ports was specified in the Demonstration Plan, on the expectation that differences in concentration would provide information about the performance of the AVOAS in measuring more than one concentration. Samples from each port were analyzed separately; i.e., samples from S-3 and S-4 were not physically combined. Water from port S-6 (treated effluent) was used to prepare spiked samples and analytical and transport blanks.

## Project Organization

The EMSL-LV and its prime contractor, Lockheed Engineering & Sciences Company (LESC), worked together to plan, conduct, evaluate, and report the results of the AVOAS demonstration. The EMSL-LV Technical Leader arranged scheduling and the approach of the demonstration. The Technical Leader was also responsible for communicating with EPA Region I staff to obtain access to the site, and for background and health and safety information. Oversight of all remedial activities at the Wells G and H Superfund Site is the responsibility of the EPA Region I Remedial Project Manager. The site remediation contractor for the potentially responsible parties is Environmental Project Control, Inc. (EPC). For the AVOAS demonstration, EPC was responsible for overseeing or conducting all of the operational aspects of the ground-water pump-and-treat process. The Johnson Company designed the treatment system. EPC arranged the subcontract with A⁺RT, Inc. to provide the on-line analytical capability.

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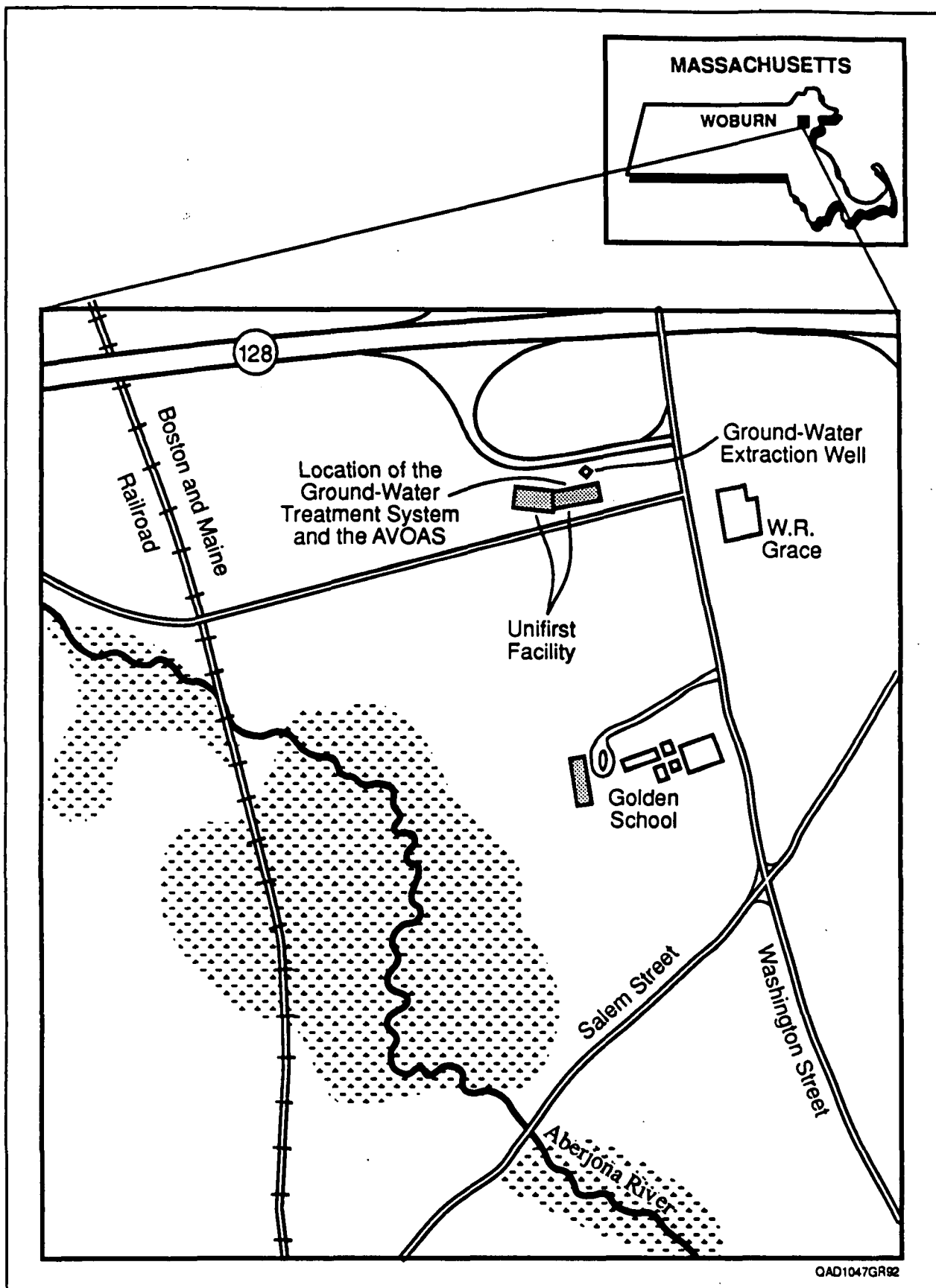
Figure 1-2. Area map of the Wells G and H Superfund Site, Woburn, Massachusetts.
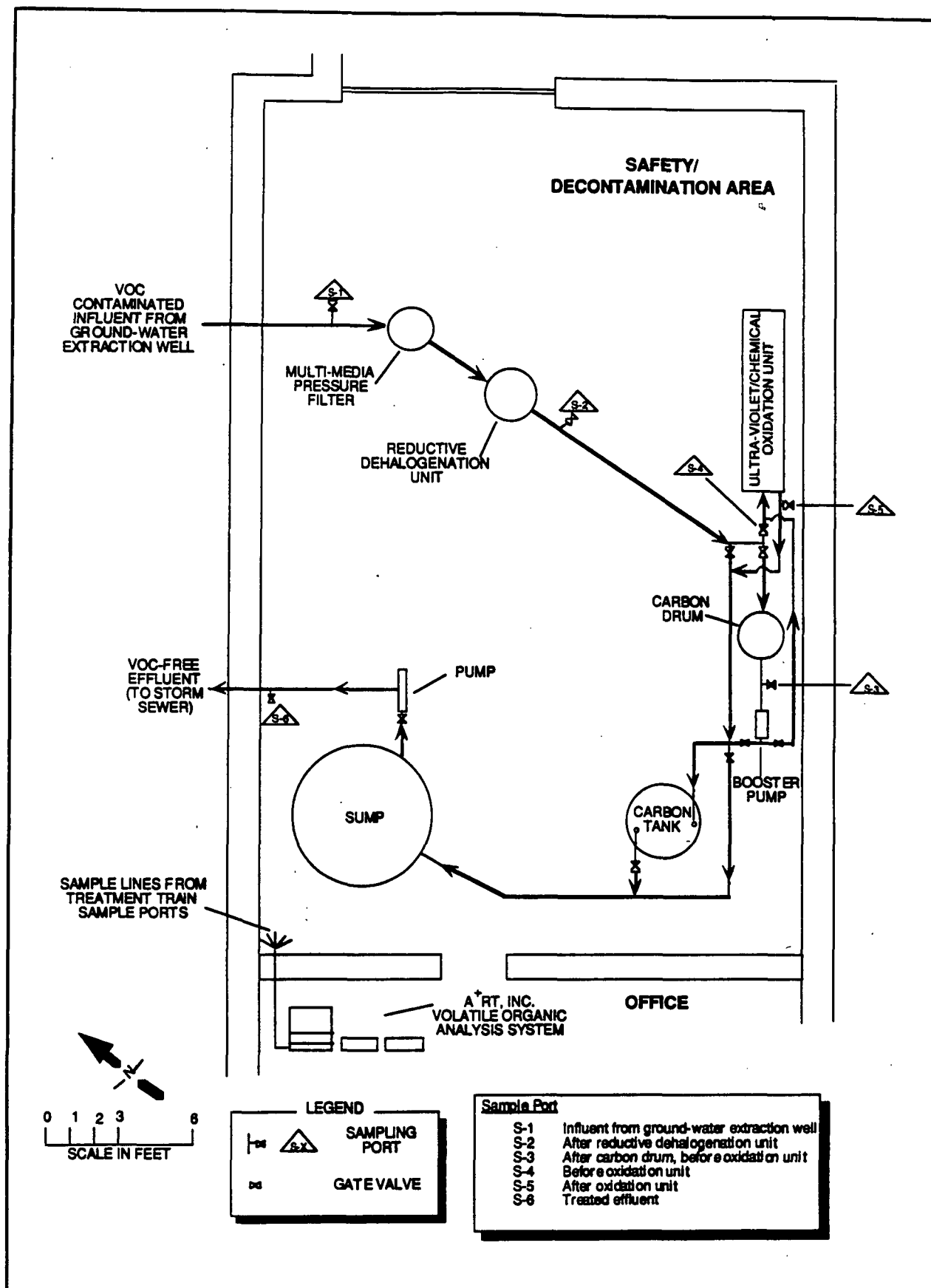
**Figure 1-3. Schematic of the Unifirst Ground-Water Treatment System.**

SAFETY/
DECONTAMINATION AREA

VOC
CONTAMINATED
INFLUENT FROM
GROUND-WATER
EXTRACTION WELL

MULTI-MEDIA
PRESSURE
FILTER

REDUCTIVE
DEHALOGENATION
UNIT

ULTRA-VIOLET/CHEMICAL
OXIDATION UNIT

CARBON
DRUM

VOC-FREE
EFFLUENT
(TO STORM
SEWER)

PUMP

BOOSTER
PUMP

SUMP

CARBON
TANK

SAMPLE LINES FROM
TREATMENT TRAIN
SAMPLE PORTS

A⁺RT, INC.
VOLATILE ORGANIC
ANALYSIS SYSTEM

OFFICE

0  1  2  3      6
SCALE IN FEET

LEGEND

SAMPLING
PORT

GATE VALVE

Sample Port
S-1    Influent from ground-water extraction well
S-2    After reductive dehalogenation unit
S-3    After carbon drum, before oxidation unit
S-4    Before oxidation unit
S-5    After oxidation unit
S-6    Treated effluent

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Figure 1-4 shows the organizational structure for the AVOAS demonstration. Key participants included:

- Statistician (LESC): Responsible for designing the evaluation and overseeing data analysis and interpretation of results, including verifying and validating data, generating data tables and plots, and programming and executing statistical routines.

- Demonstration Design Consultant (EPA Cooperative Agreement, University of Houston): Assisted in the development of the AVOAS dem-



EMSL-LV - Environmental Monitoring Systems Laboratory-Las Vegas
LESC - Lockheed Engineering & Sciences Company
QA - Quality Assurance
SITE - Superfund Innovative Technology Evaluation
A+ RT, Inc. - Analytic and Remedial Technology, Inc.
EPC - Environmental Project Control, Inc.
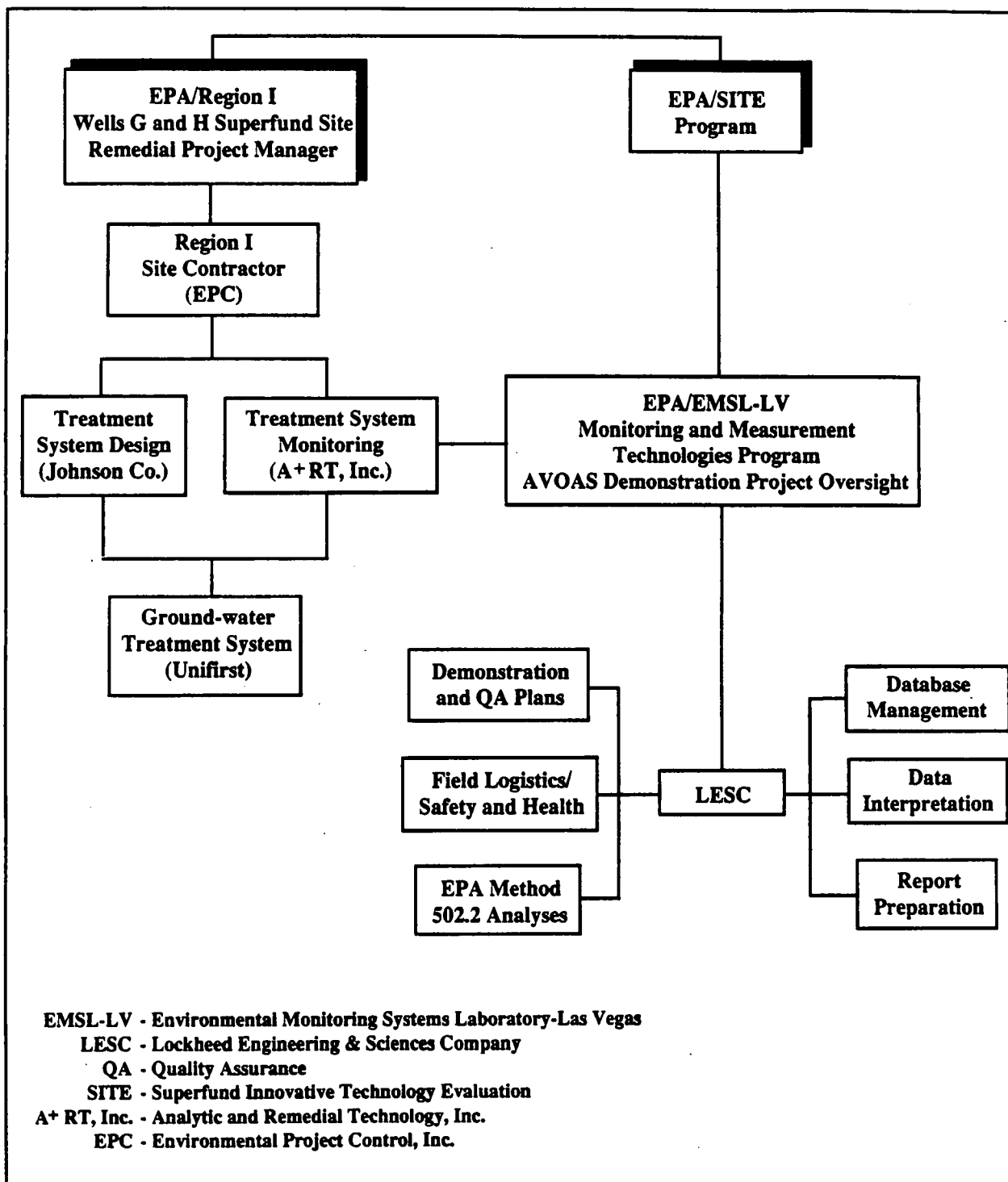
Figure 1-4. Organizational Structure of the AVOAS Demonstration.

onstration design. Provided data interpretation and report review.

- Supervising Chemist (LESC): Responsible for ensuring the technical and scientific quality of the project. Responsible for overseeing or performing technical activities related to planning and conducting the evaluation and interpreting results, including overseeing field and reference laboratory operations, preparing sample spikes, and approving any modifications to the Demonstration Plan.

- AVOAS Developer (A$^+$RT, Inc.): Responsible for installing and operating the AVOAS at the field site, including calibrating the instrument, collecting treatment train samples, analyzing samples, and providing copies of the data generated by the AVOAS.

- Project QA Manager (LESC): Responsible for developing the QAPjP and for overseeing the review and interpretation of the QA data.

- Logistics and Sampling Coordinator (LESC): Responsible for all aspects of field operations, including site reconnaissance, sample collection and shipment, sample chain-of-custody, decontamination of equipment and disposal of hazardous wastes in the field, and documentation of field activities.

- Laboratory Analyst (LESC): Responsible for analyzing samples in accordance with EPA Method 502.2 and with the Demonstration Plan and the QAPjP, and for documenting and reporting data in the required format.

- Data Base Manager (LESC): Responsible for the acquisition and formatting of all data generated.

- Health and Safety Coordinator (LESC): Responsible for ensuring that all field and laboratory health and safety issues were addressed, and for preparation and approval of the Site Safety and Health Plan.

- Report Coordinator and Writer (LESC): Responsible for coordinating input from project participants and preparing this report.

# Section 2
## AVOAS Demonstration Design and Activities

## Demonstration Design

### Rationale Behind the AVOAS Demonstration Design

An important objective of the AVOAS demonstration design was to account for factors that could affect the comparability of results. These included: 1) sample-related factors, including sample matrix effects and changes in sample integrity during collection, preservation, transport, and storage and 2) variability due to analysis, including differences in instrument hardware and function, day-to-day variation in operating conditions, drift in instrument calibration, and variability in the laboratory technique of different analysts.

### Sources of Variability in Samples

*Sample Matrix Effects* — Chromatographic retention times and measured concentrations of target analytes can be affected by the chemical and physical characteristics of the sample, i.e., the sample matrix. Matrices in this demonstration included 1) reagent-grade water for making the standards for the initial calibration and for the daily instrument calibration checks and 2) ground-water treatment system (i.e., treatment train) water. To reduce the potential variability due to matrix, treatment train effluent water from port S-6 was purged to remove VOCs and was used for travel blanks, AVOAS instrument blanks, and for preparing spiked samples.

*Changes in Sample Integrity* — Sample integrity refers to how well the sample composition and concentration at the time of analysis reflect those characteristics at the time the sample was collected. For demonstrations in which two methods are being compared, maintaining uniformity in the sample pairs analyzed by the test and the comparison method is critical for comparing data from both methods. Sample integrity can be compromised by collection procedures, sample

container characteristics, conditions during shipping (e.g., temperature or barometric pressure changes), component degradation or alteration (e.g., due to biological or photochemical processes), and handling steps during analysis. Maintaining the integrity of samples containing low-molecular-weight chlorinated hydrocarbons, the target analytes for the AVOAS demonstration, is a particular challenge because those compounds can easily volatilize into the atmosphere or sorb to container materials. In addition, residues in sample containers or in the atmosphere in which the samples are stored can contaminate samples, leading to biased or false-positive results (e.g., increased concentrations or the presence of compounds not actually present in the medium sampled).

The potential for changes in sample integrity was a concern for samples shipped to EMSL-LV, because they required additional handling steps and time between sampling and analysis. To minimize variability, the guidelines of Method 502.2 for collecting, preserving, shipping, and handling samples containing VOCs were followed. In addition, holding time — the time between sample collection and analysis — was minimized as much as possible. A transport study was performed in which results for samples spiked with known analyte concentrations and shipped, were compared with results for corresponding samples not shipped.

### Sources of Analytical Variability

*Differences in Instrument Hardware and Operation* — The manner in which the AVOAS collects and handles samples when operated in the automated ("on-line" mode) did not permit direct comparison of sample results with those of Method 502.2. In the on-line mode, the AVOAS conveys samples from the sampling ports to the analytical system. Samples are introduced directly into the injector without exposure to the atmosphere, and are analyzed immediately. In contrast, the estab-

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lished methods, including Method 502.2 involve manual collection of samples into containers, transport to a laboratory, and refrigerated storage prior to analysis. The sample is exposed to the atmosphere during collection, and usually again just before analysis. To help identify any effects on the data due to these inherent differences in procedure, the AVOAS was used in both the on-line, automated mode and in off-line mode for analysis of treatment train samples. For the off-line procedure, the line between the manifold and injector was momentarily opened and placed in the sample vial. The sample water was then pumped through the sampling loop of the AVOAS injector.

Another difference between the AVOAS and typical Method 502.2 analyses is the means by which sample concentrations are adjusted to fall within the linear range of the detector. The AVOAS injector uses sampling loops of different volumes that can be selected to adjust for analyte concentrations. For example, for high-concentration samples, a small sample volume is used so that a small quantity of analyte is introduced into the analytical system. By contrast, the standard purge-and-trap apparatus used with the EMSL-LV instrument makes all injections using the same sample volume. Adjustments to keep the sample concentration range within the linear range of the detector are made by diluting the sample. For this demonstration, sample dilution was required to bring the highest concentration analyte, PCE, to within the linear range of the EMSL-LV detector. Potential sources of variability in the EMSL-LV data arise from the dilution procedure, and for the AVOAS data, from the performance of the sampling loops.

Finally, the method by which the AVOAS strips VOCs from samples (A$^+$RT, Inc. proprietary) is different from standard purge-and-trap techniques, so that differences in VOC stripping efficiency are possible. Although this difference should be compensated for through analysis of standards, stripping efficiency for the different sample loop sizes may vary; this source of variability was not evaluated in this demonstration.

*Day-to-Day Variations in Instrument Operating Conditions* — Day-to-day variability in instrument operating conditions could arise from several sources. The GC used in this demonstration with the AVOAS is very basic in design. It was installed on location at the industrial facility where the ground-water treatment system is housed. The demonstration began within 3 days after the AVOAS was installed. During the demonstration,

in addition to processing SITE demonstration samples, the AVOAS was used in the on-line monitoring mode and for off-line analyses of samples from a second treatment system. The AVOAS was operating for over 22 hours per day during the demonstration. Samples of widely varying concentrations were analyzed sequentially, providing the potential for contaminant carryover from high-concentration samples. In contrast, the EMSL-LV instrument had been allowed to stabilize in the laboratory for nearly 2 weeks prior to the demonstration. Only AVOAS demonstration samples were analyzed by that instrument during this study, and the instrument was used less than 8 hours per day.

To help detect day-to-day sources of variability, quality control check standards, continuing calibration check standards, and instrument blanks were analyzed daily. To identify effects due to the time of day, treatment train samples were collected and analyzed by the AVOAS in both the morning and the afternoon.

*Drift in Instrument Calibration* — Changes in instrument response factors or calibration curves can be a significant source of measurement variability in VOC analysis. Both the AVOAS and EMSL-LV instruments were calibrated prior to the demonstration, and their calibration was monitored daily using the CCCS.

*Other Sources of Variability* — Data for spiked samples can have inherent variability. For example, analyst spiking technique can vary, and actual concentrations of spiking solutions can be different from intended concentrations. To minimize these sources of variability, the stock solutions for spiked samples were prepared in batches and sealed in ampoules by one chemist before the study. Spiked samples and sample aliquots were prepared by the same chemist at the field site.

## AVOAS Demonstration Evaluations

The assessment of the AVOAS performance relative to that of Method 502.2 was based on three evaluations, which are depicted schematically in Figure 2-1 and are described below.

1. The true concentrations of VOCs in the ground-water treatment train water were unknown. Therefore, to assess the comparability of results obtained by the AVOAS and by Method 502.2, samples spiked with known concentrations of analytes (i.e., spiked purged effluent water samples) were prepared at the field site and were analyzed by both instruments. Data were gener-
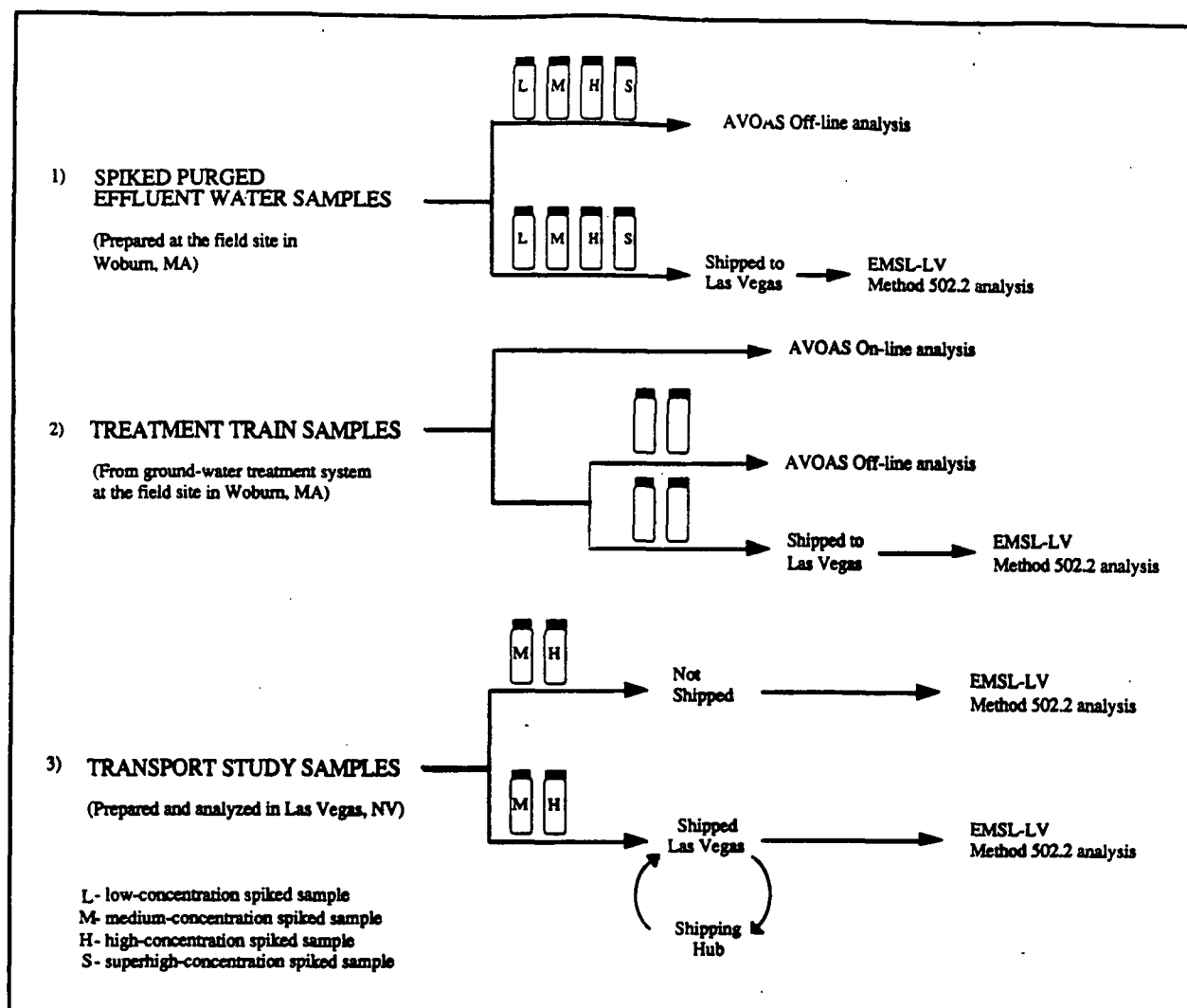
**Figure 2-1. AVOAS Demonstration Evaluations.**

ated for nine compounds in four concentration ranges, designated as low, medium, high, and superhigh.

2. To estimate differences between on-line and off-line modes of analysis by the AVOAS, treatment train samples were analyzed in both modes and the results were compared. These results were also compared with those generated off-site by the EMSL-LV instrument. Data for two different sample ports (S-3 and S-4) and for two times of analysis were collected. Seven volatile chlorinated compounds were present in detectable concentrations in these samples.

3. A transport study was performed to compare results for samples shipped with those for samples not shipped. This study was done after the demonstration, and all analyses were done at EMSL-LV. Samples spiked with known con-

centrations of analytes were used, and data for two concentration ranges and for two different analysts were generated.

Quality control (QC) samples were analyzed for all evaluations to ensure data of known quality for each of the assessments. In addition, a linearity study of the AVOAS instrument response was performed using the spiked sample results.

## Demonstration Components

### Sample Types Analyzed

The types of samples used in the AVOAS demonstration are summarized in Table 2-1, and methods for their preparation are described below. Table 2-2 summarizes analyte concentrations for each sample type.

**TABLE 2-1. SAMPLE TYPES ANALYZED FOR THE AVOAS DEMONSTRATION**

| Sample Name | Sample Description | Use | Purpose |
|---|---|---|---|
| Purged Effluent Water (PEW) | Water from treatment train sample port S-6, purged to remove VOCs | For making up matrix spike samples for analysis by the AVOAS and by EMSL-LV.<br><br>As a blank sample for the AVOAS and as a travel blank for samples shipped to EMSL-LV.<br><br>For making up matrix spike samples analyzed by EMSL-LV for the transport study. | To minimize variability due to matrix effects of the treatment train water. |
| Spiked Purged Effluent Water (SPEW) | Purged effluent water spiked with nine compounds in four concentration ranges; analyzed by the AVOAS (off-line) and EMSL-LV. SPEW samples were made in the field from ampoules of stock solutions prepared prior to the demonstration. | To compare the accuracy and precision obtained by the AVOAS (off-line) and by EMSL-LV.<br><br>In the transport study, to compare results between transported and non-transported samples. | To provide samples of known concentration in a variety of concentration ranges. |
| Treatment Train (TT) | Samples from treatment train ports S-3 and S-4, analyzed by the AVOAS (on-line and off-line) and EMSL-LV. | To determine whether AVOAS off-line results are representative of AVOAS on-line results<br><br>To compare AVOAS and EMSL-LV measurement performance | To provide actual environmental samples. |
| Quality Control Check Standard (QCCS) | QC standard required by EPA Method 502.2 containing 5 VOCs at low and very low μg/L levels, analyzed by both the AVOAS and EMSL-LV. | To indicate any loss of instrument sensitivity. | To provide samples of known concentration so that instrument performance can be monitored. |
| Continuing Calibration Check Standard (CCCS) | A calibration check standard analyzed daily by both the AVOAS and EMSL-LV. | To verify instrument performance in terms of response factors. | To provide samples of known concentration so that ongoing instrument performance can be monitored. |

## Treatment Train Samples

The protocol for collection of treatment train (TT) samples was as follows: Each morning during the routine AVOAS on-line collection and analysis of a sample from port S-3 or S-4, water from the port sampled AVOAS was also collected automatically into four 40-mL volatile organic analysis (VOA) vials. The first vial collected was analyzed by the AVOAS immediately after the on-line analysis of the same sample, using the off-line procedure. The TT samples for EMSL-LV were preserved by acidifying to pH<2 with HCl. In the afternoon, the alternate port (S-3 or S-4) was sampled in the same fashion. Both morning and after-noon TT samples were shipped that day to EMSL-LV by overnight express carrier.

## Purged Effluent Water

Purged effluent water (PEW) was prepared as follows: Four gallons of water from sampling port S-6 (final effluent) was collected into a 5-gallon Pyrex solution bottle on May 16 and was purged continuously using high-purity helium gas. The purged water was poured into four 1-L bottles and was analyzed in the field using the AVOAS instrument to verify the absence of VOCs. Three 1-L bottles of the purged water were sent to EMSL-LV for use in the transport study. The remaining liter

**TABLE 2-2. SUMMARY OF ANALYTE CONCENTRATIONS (µg/L), BY SAMPLE TYPE**

| Compound | Treatment Train[a] Port S-3 | Treatment Train[a] Port S-4 | Spiked Purged Effluent Water[b] Low | Spiked Purged Effluent Water[b] Medium | Spiked Purged Effluent Water[b] High | Spiked Purged Effluent Water[b] Super High | QCCS[b] EMSL-LV and AVOAS | CCCS[b] EMSL-LV | CCCS[b] AVOAS | Transport Study[b] Medium | Transport Study[b] High |
|---|---|---|---|---|---|---|---|---|---|---|---|
| vinyl chloride | ND | ND | 22.4 | 37.4 | 224 | 747 | 20.0 | 20 | 400 | 37.4 | 227 |
| 1,1-dichloroethene | 6.7 | 5.9 | 4.6 | 91.1 | 45.6 | 0 | 2.0 | 20 | 400 | 91.1 | 45.6 |
| trans-1,2-dichloroethene | 0.68[c] | 0.82[c] | 13.8 | 97.5 | 138 | 1946 | 0 | 20 | 400 | 97.5 | 138 |
| 1,1-dichloroethane | 3.6[c] | 3.0[c] | 9.1 | 45.6 | 91.1 | 911 | 0 | 20 | 400 | 45.6 | 91.1 |
| cis-1,2-dichloroethene | 19 | 13 | 28.1 | 23.7 | 281 | 467 | 0 | 20 | 400 | 23.7 | 281 |
| 1,1,1-trichloroethane | 37 | 31 | 9.1 | 91.1 | 91.1 | 1822 | 10.0 | 20 | 400 | 91.1 | 91.1 |
| 1,2-dichloroethane | ND | ND | 9.0 | 39.2 | 90.2 | 788 | 20 | 400 | 400 | 39.2 | 90.2 |
| trichloroethene | 75 | 60 | 213 | 53.8 | 213 | 1067 | 2.0 | 20 | 400 | 53.8 | 213 |
| tetrachloroethene | 2583 | 2550 | 23.7 | 88.7 | 237 | 1774 | 15.0 | 20 | 400 | 88.7 | 237 |

ND: Not detected by either the AVOAS or EMSL-LV.
CCCS: Continuing calibration check standard.
QCCS: Quality control check standard.
[a] Mean concentration, µg/L. Values are approximate and are mean values for all samples collected (a.m. and p.m.) by the AVOAS over the 6-day demonstration.
[b] Target concentration, µg/L.
[c] Detected by AVOAS, but not by EMSL-LV.

was used to prepare the spiked samples and was also used as an instrument blank for the AVOAS.

## Spiked Purged Effluent Water

Spiked purged effluent water (SPEW) samples were freshly prepared each day of the demonstration at the field site. The solutions used to spike the PEW had been prepared for each of four spiking concentration ranges and sealed in glass ampoules at EMSL-LV prior to the field demonstration. New ampoules were opened daily to prepare SPEW samples, and the spiking procedure was performed by the same chemist to minimize variability due to spiking technique. To prepare each SPEW sample, a 40-mL VOA vial was filled most of the way with PEW. The spiking solution was added directly into the VOA vial using a micropipette. Purged effluent water was added to fill the vial, and the vial was capped immediately and checked for bubbles. If bubbles were present, the vial was discarded, and a fresh spiked sample was prepared.

Duplicate spike-sample vials were made from the same ampoule. One sample vial of each concentration range was analyzed by the AVOAS in the off-line mode, generally within 1 hour of preparation. The other aliquots were preserved (acidified with HCl to pH<2), chilled at 4 °C, and shipped to EMSL-LV in coolers. The aliquot analyzed in the field was not preserved.

To help maintain analyst objectivity, neither the AVOAS nor the EMSL-LV analysts were informed beforehand of the exact SPEW spiked concentrations.

## Performance Evaluation Study

A performance evaluation (PE) study was conducted prior to the demonstration on behalf of EPC, Inc. by Trillium, Inc. The PE study had two objectives: 1) the determination of method detection limits (MDLs) and practical quantitation limits (PQLs) for both the EMSL-LV and A⁺RT, Inc. instruments for each of the nine analytes targeted for the AVOAS demonstration and 2) the analysis of "blind" (i.e., the composition and concentration

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are unknown to the analyst) samples, to provide an impartial determination of instrument performance in measuring low (ppb level) concentrations of analytes. EMSL-LV analyses were performed using modified EPA Method 502.2 procedures. For the AVOAS analyses, the PE samples were introduced in the sample manifold in the off-line mode. At the time of the PE study, the AVOAS was not yet installed at the field site, so the PE samples were analyzed at the A⁺RT, Inc. research and development facility.

## Determination of Method Detection and Practical Quantitation Limits

The MDL of a method is defined as its performance in measuring an analyte in a sample matrix, regardless of the sample's origin (Glaser et al., 1981). For the PE study, the MDL was set as three times the standard deviation of the analytical

results for seven replicate analyses, in µg/L. The PQL was set as 10 times the MDL.

A representative ground-water sample was used by each laboratory to make spiked samples for the MDL and PQL determinations. The spiking concentration of each analyte was 1 µg/L. Seven replicates each of spiked and unspiked aliquots were analyzed alternately, and the MDLs and PQLs were calculated for each compound. Table 2-3 gives the EMSL-LV and A⁺RT, Inc. MDLs for each sample type analyzed for the demonstration. The MDLs for the AVOAS depended on sample volume, as determined by sample loop size. In the Trillium, Inc. study, the 10.0-mL sample loop was used on the AVOAS, and MDLs were calculated for the other loop volumes. The MDLs for the EMSL-LV instrument depended on the dilution factor used.

**TABLE 2-3. SUMMARY OF METHOD DETECTION LIMITS (µg/L) FOR THE AVOAS AND EMSL-LV INSTRUMENTS, BY SAMPLE LOOP SIZE, DILUTION, AND SAMPLE TYPE**

| | AVOAS[a] | | | | EMSL-LV | | |
|---|---|---|---|---|---|---|---|
| | 10-mL Loop | 5-mL Loop | 1.0-mL Loop | 0.2-mL Loop | No Dilution | 1:10 Dilution | 1:100 Dilution |
| Compound | B, L Samples | M, QCCS Samples | H Samples | S, TT Samples | B, L, M, QCCS Samples | H Samples | S, TT Samples |
| vinyl chloride | 0.08 | 0.16 | 0.8 | 4.0 | 0.08 | 0.8 | 8.0 |
| 1,1-dichloroethene | 0.05 | 0.1 | 0.5 | 2.5 | 0.16 | 1.6 | 6.0 |
| trans-1,2-dichloroethene | 0.01 | 0.02 | 0.1 | 0.5 | 0.17 | 1.7 | 17 |
| 1,1-dichloroethane | 0.02 | 0.04 | 0.2 | 1.0 | 0.08 | 0.8 | 8.0 |
| cis-1,2-dichloroethene | 0.02 | 0.04 | 0.2 | 1.0 | 0.24 | 2.4 | 6.0 |
| 1,1,1-trichloroethane | 0.07 | 0.14 | 0.7 | 3.5 | 0.12 | 1.2 | 23 |
| 1,2-dichloroethane | 0.05 | 0.10 | 0.5 | 2.5 | 0.19 | 1.9 | 19 |
| trichloroethene | 0.03 | 0.06 | 0.3 | 1.5 | 0.22 | 2.2 | 22 |
| tetrachloroethene | 0.01 | 0.02 | 0.1 | 0.5 | 0.3 | 3.0 | 30 |

[a] *Method Detection Limits (MDLs) were measured using the 10-mL loop; MDLs for the other loop sizes were calculated from those values.*
*For the demonstration, each sample type was analyzed using the loop or dilution indicated in the table headings:*

B:      *Blank*
L:      *Low-concentration spiked purged effluent water sample.*
M:      *Medium-concentration spiked purged effluent water sample.*
H:      *High-concentration spiked purged effluent water sample.*
S:      *Superhigh-concentration spiked purged effluent water sample.*
QCCS:   *Quality control check standard.*
TT:      *Treatment train sample.*

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## Analysis of Blind Performance Evaluation Samples

Two PE samples were sent to each of the participating laboratories by Trillium, Inc. Each of the two samples was provided in three 40-mL vials and a 1-L bottle. The compounds in one of the samples were present at concentrations of approximately 1.7 to 2.5 µg/L, and in the other at approximately 0.1 to 0.6 µg/L. Trillium, Inc. determined that the EMSL-LV and AVOAS results were comparable.

## Transport Study

The effect of shipping on sample integrity was supposed to be studied concurrently with the AVOAS demonstration, using the AVOAS to analyze transported and nontransported samples. However, scheduling commitments for the AVOAS required the transport study to be delayed to a later date. The transport study was performed from May 30 to June 13, using the EMSL-LV instrument for all comparisons, as described below.

The spiked samples used for the transport study were made in the same manner as the SPEW samples, using the PEW that had been shipped to EMSL-LV during the demonstration and stock-solution ampoules originally intended for the Woburn transport study. Two concentration ranges, medium and high, were tested. Four 40-mL VOA vials of each of the two concentration ranges were prepared daily for 5 days, using fresh ampoules each day. Two vials from each concentration range were shipped and a corresponding set was not shipped. The transported vials were preserved by acidifying to pH<2; the nontransported vials were not. The transported vials were shipped in coolers at approximately 4 °C in the same manner as the demonstration samples had been, using the same overnight carrier service (Federal Express). Samples were sent from Las Vegas to the central Federal Express shipping hub, and were returned the following morning to Las Vegas. Nontransported samples were analyzed within 6 hours of preparation; transported samples were analyzed within 30 hours of preparation. For the first 3 days of the study the samples were prepared and analyzed by one chemist, and for the last 2 days by a different chemist.

## Quality Assurance for the AVOAS Demonstration

The purpose of the QA program for the AVOAS demonstration was to ensure that the qual-ity of data produced would be sufficient to allow formulation of sound conclusions about the performance of the AVOAS relative to the comparison method.

According to the description of project categories specified in the EMSL-LV Quality Assurance Program Plan (U.S. EPA, 1987), the AVOAS demonstration is considered a Category II project. Category II projects apply to measurement activities whose results are used by a client organization, but not directly in regulatory, enforcement, legal, or policy matters. The QAPjP addressed the key elements required for Category II projects, and was prepared in accordance with the guidance in Preparation Aids for the Development of Category II Project Plans (U.S. EPA, 1991). The QAPjP clearly identified and delegated responsibilities related to all aspects of QA for this demonstration, defined data quality objectives (DQOs), and described the measures required to achieve the DQOs.

### Data Quality Objectives

The EPA recommends that DQOs include, at a minimum, five indicators of data quality (Stanley and Verner 1983): representativeness, completeness, comparability, accuracy, and precision. Table 2-4 summarizes the DQOs for the AVOAS demonstration.

DQOs were set to ensure that the study was well enough designed and carried out for the comparisons to be as free from confounding and extraneous sources of variability as possible. In addition, because a fair assessment of the AVOAS required that the performance of Method 502.2 be known, it was important that DQOs be specified for that method. DQOs were not set for the AVOAS because the performance of that system was unknown and its assessment was an objective of the demonstration.

*Representativeness* — Representativeness is defined as "the degree to which the data accurately and precisely represent a characteristic or a parameter, variation of a property, a process characteristic, or an operation condition" (Stanley and Verner, 1985). Representativeness was a particular issue in this demonstration because the AVOAS is designed to collect samples directly from a water treatment stream with no manual intervention. In normal operations, the samples are never exposed to air. For this demonstration, analysis of spiked samples (i.e., the SPEW, QCCS, and CCCS samples) by the AVOAS required that the operator disconnect the

sample line and introduce the samples in the off-line mode. An estimate of the degree of representativeness of spiked samples was made by comparing the results of TT samples analyzed on-line and off-line by the AVOAS and by EMSL-LV. Representativeness was optimized by using consistent sample collection and preparation techniques and by taking measures to ensure that sample integrity was maintained to the highest degree possible.

*Completeness* — The completeness of a data set can be reduced by contamination, loss of samples due to vial breakage, and problems with calibration, among other things. Completeness can be monitored through use of appropriate QC samples, i.e., instrument and travel blanks, CCCSs, and QCCSs. The AVOAS demonstration plan was designed to ensure maximum use of the resulting data. Because each analysis provided more than one type of data, for both QC and statistical analysis purposes, the completeness objective for this demonstration was 100%.

*Comparability* — Comparability is defined as "the confidence with which one data set can be compared to another" (Stanley and Verner, 1985). Analytical results from SPEW, TT, and QC samples were used to evaluate the comparability of the two methods.

*Accuracy* — Accuracy refers to the degree of agreement of a measured value with the true, or reference value for each analyte (Taylor, 1987). Accuracy was assessed using data from daily analyses of SPEW and QCCS samples and, for EMSL-LV analyses, surrogate compound recoveries. Accuracy was computed as the percent recovery (%R) of measured concentrations relative to spiked (target) concentrations for each analyte:

$$\%R = 100 \times C_m/C_t$$

where:

$C_m$ = measured concentration of analyte ($\mu$g/L)

$C_t$ = target concentration of analyte ($\mu$g/L)

### TABLE 2-4. DATA QUALITY OBJECTIVES FOR THE AVOAS DEMONSTRATION

| DQO Element | Demonstration Purpose | Computation | DQO |
|---|---|---|---|
| Representativeness | Assesses how well off-line AVOAS measurements represented on-line AVOAS measurements to determine whether on-line AVOAS and EMSL-LV measurements could be compared. | Difference in mean %R for on-line and off-line treatment train samples. Analysis of variance. | None set. |
| Completeness | Assesses the amount of useable data collected. | %C | 100% |
| Comparability | Determines how well AVOAS and EMSL-LV data compare. | | None set. |
| | SPEW samples: off-line AVOAS/EMSL-LV. | • %R <br> • Difference in mean %R. | |
| | TT samples: On-line AVOAS/off-line AVOAS. On-line AVOAS/EMSL-LV. Off-line AVOAS/EMSL-LV. | Difference in mean %R. | |
| Accuracy | Compares agreement of AVOAS measurements with target concentrations and with EMSL-LV measurements. | %R | %R within 100 ±30% for Method 502.2* |
| Precision | Compares variability among replicate measurements for the AVOAS and EMSL-LV. | %RSD | %RSD ≤30% for Method 502.2* |

%R:  Percent recovery, computed as $\%R = (C_m/C_t) \cdot 100$, where $C_m$ = measured analyte concentration ($\mu$g/L),
    $C_t$ = target analyte concentration ($\mu$g/L).
Difference in mean %R: Difference in mean percent recovery, computed as mean %R for data set 1 minus mean %R for data set 2.
%RSD:  Percent relative standard deviation, computed as %RSD = (standard deviation/mean) • 100.
%C:  Percent completeness, computed as %C = 100 • V/n, where
    V = number of valid measurements, n = total number of measurements.
* DQOs were not set for the AVOAS because the performance of that system was unknown and its assessment was an objective of the demonstration.

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The accuracy DQO for the EMSL-LV instrument, based on Method 502.2 performance data and on performance data presented in a document evaluating various water analysis methods (EPA, 1988), was 100 ±30%R for measured concentrations relative to target concentrations of spiked compounds.

*Precision* — Precision is defined as the degree of mutual agreement among individual measurements (Taylor, 1987). Precision values were computed for each compound and each sample type over the 6 days of the demonstration for the AVOAS on-line and off-line and the EMSL-LV measurements. Precision for this demonstration was expressed as percent relative standard deviation (%RSD), calculated as:

$$\%RSD = (\sigma/\mu) \times 100$$

where:

$\sigma$ = standard deviation

$\mu$ = mean value of results over the 6 days of the demonstration

The precision DQO for Method 502.2 analyses was ≤30 %RSD.

## Instrument Calibration

The AVOAS and EMSL-LV instruments were calibrated within 2 days before the start of the demonstration. A 5-point calibration curve was used for the AVOAS, and a 4-point calibration curve was used for the EMSL-LV instrument. To monitor instrument response during the demonstration, single-point calibration checks were performed daily using the CCCSs. The calibration standards for both instruments came from the same supplier and lot so as to eliminate potential variability due to differences in concentration that can occur in stock solutions from different sources.

The performance, expressed as percent difference (%D) between the initial and continuing calibration responses for each analyte, was calculated as follows:

$$\%D = (C_1 - C_2) \times 100 / C_1$$

where:

$C_1$ = response in the initial calibration

$C_2$ = response in each continuing calibration

A 20% difference between initial and continuing calibration was set as the acceptance criterion for the EMSL-LV instrument.

## Quality Control Samples

*Quality Control Check Standard* — To monitor instrument sensitivity and performance, the QAPjP required daily analysis of a quality control check standard (QCCS) by each instrument. QCCSs were made from commercially prepared stock standards (Restek) having certified concentrations of five target analytes. The QCCS samples for the AVOAS were made daily at the field site by the LESC supervising chemist using PEW; a new ampoule of stock standards was used each day. The QCCS for the EMSL-LV instrument was made by the EMSL-LV analyst using reagent-grade water; the same stock solution ampoule was used for the duration of the demonstration.

*Continuing Calibration Check Standards* — The QAPjP required daily analysis of continuing calibration check standards (CCCSs), to provide an ongoing indication of instrument performance. CCCSs were one of the standards that had been used to calibrate the instruments prior to the demonstration. For the EMSL-LV instrument, the CCCS concentration was 20 µg/L; for the AVOAS, it was 400 µg/L. The CCCS for the AVOAS was made daily by the AVOAS operator from a fresh stock standard ampoule; the EMSL-LV daily check was performed using a standard prepared at the beginning of the demonstration.

*Instrument Blank Samples* — Instrument blanks were samples of VOC-free water (PEW, reagent-grade water, or VOC-free water from sample port S-6) analyzed to verify that the analytical systems were not contaminated. For the systems to be considered free of contamination, target analyte concentrations were required to be below the low-concentration SPEW sample or the MDL, whichever was less.

*Travel Blank Samples* — Travel blank samples were used to determine whether routine samples may have been contaminated during shipping or handling. Travel blanks were unspiked PEW sent with each batch of TT and SPEW samples to EMSL-LV. Travel blank samples were also used in the transport study.

## Demonstration Methods

### EPA Method 502.2 Requirements and Modifications

The procedures for instrument setup, initial calibration, continuing calibration checks, additional QA/QC measures, and associated corrective

actions are specified in EPA Method 502.2 and are summarized in Table 2-5. Some modifications to the method were used for this demonstration:

1. Method 502.2 requires the use of a photoionization detector (PID). and electrolytic conductivity detector (ELCD). in series. The AVOAS instrument was used with only the ELCD because the target analytes in this study were halogenated hydrocarbons, which are best measured using this detector. Both PID and ELCD were used with the EMSL-LV instrument; however, the PID served only as an operator performance guide, and the PID data were not included in the demonstration database.

2. Compounds with chromatographic retention times greater than that of PCE were not detected in any of the samples. Therefore, the analytical run times were shortened to increase sample throughput (i.e., the number of samples that can be analyzed in a given amount of time).

3. Method 502.2 requires that reagent water fortified with target analytes at low concentrations (just above the method PQLs). be analyzed as a laboratory-fortified blank once each day or once every 20 samples. This QC procedure was not included in the demonstration, since five of the eight daily analyses were performed on spiked water samples.

### TABLE 2-5. METHOD 502.2 QUALITY CONTROL REQUIREMENTS

| QC Element | Specifications | Acceptance Criteria | Corrective Action |
|---|---|---|---|
| 1. Initial calibration | All target compounds and surrogate(s) at three-five concentration levels | < 10% RSD over concentration range required to use mean RF for quantitation | Plot calibration curves for analytes with RSDs >10% |
| 2. Continuing calibration verification | One or more standards analyzed on each working day | RF or response (height or area) for each analyte ± 20% of RF or response for that analyte in the initial calibration standard | • Repeat the test using a fresh standard<br>• If test fails, recalibrate or prepare a new curve |
| 3. Initial demonstration of precision and accuracy<br>Note: These analyses were performed as part of the PE study. | Four to seven replicates of a low level (0.5 - 5 µg/L) water sample | • The mean accuracy (% recovery) should be 80 - 120 %, and the %RSD should be < 20 %<br>• The MDL must be sufficient to detect analytes at the regulatory levels | Perform new initial calibration or perform maintenance, and rerun the analyses |
| 4. Quality Control Check Standards (commercially prepared) | • Analyze once each day at the end of sample analysis<br>• Compounds at concentrations known to analysts | • Recommended recoveries are 70 -130 %<br>• Monitor any loss of instrument sensitivity over the day, based on low-level analyte recoveries | None specified, limits are advisory |
| 5. Instrument/reagent blank | • Daily, prior to standard or sample analysis<br>• Following samples containing analytes > the high standard | No analytes present >MDL or low level standard, which ever is less | • Repeat until blank meets the acceptance criteria<br>• Decontaminate instrument |
| 6. Purged effluent water blank | • One per sample shipment batch<br>• Trip blank for laboratory samples | No analytes present >MDL or low level standard, which ever is less | None specified, flag sample results with "B" |
| 7. Surrogate | • In each blank, TT sample, spiked sample, and standard<br>• 2-bromo-1-chloropropane | Recommended recovery is 80 -120 % | • Check calculation, standard solution<br>• No other specified, flag associated sample data as estimated, "J" |

%RSD: % Relative standard deviation
MDL: Method Detection Limit
RF: Response factor
TT: Treatment Train

4. A surrogate compound was not included in the QC requirements for the AVOAS, because a sample containing a surrogate could not be introduced into the AVOAS in the on-line mode.

## Sample Analysis

Table 2-6 summarizes the components and operating conditions used for the AVOAS and EMSL-LV analytical systems during the demonstration.

## AVOAS

A Scientific Research Instruments Model 8610 GC equipped with a Tremetrics Model 1000 ELCD was used with the AVOAS for the field demonstration. The GC signal integrator was a Spectra-Physics, Model SP4400. An IBM-compatible 286 microcomputer was used to control the operation of the analytical system and to collect and store the analytical data. The AVOAS was operated at the field site by its inventor. Off-line TT samples were generally analyzed immediately after collection. SPEW samples were analyzed within several hours of preparation.

## EMSL-LV Method 502.2 Analyses

EMSL-LV analyses were performed using a Hewlett Packard (HP) Model 5890 Series 2 GC with an OI Model 4420 ELCD. The purge-and-trap unit was an OI Model 4460 with an MPM-16 autosampler. The integrator was an HP 3396. All analyses for the demonstration were performed by the same analyst, who was experienced in operation of the instrument. Samples were received the morning following shipment from Woburn and were usually analyzed that day. Exceptions were samples from the first day of the demonstration were analyzed by EMSL-LV 2 days after they were shipped from Woburn, and those from the last day were analyzed 4 days after they were shipped.

## Data Management

Data for both the AVOAS and EMSL-LV were handwritten onto forms. The AVOAS data were checked for compound identification and integration errors, completeness, and consistency at the field site by the AVOAS operator. EMSL-LV results were checked initially by the LESC analyst and were reviewed by the project QA manager. Hard copies of the chromatograms and corresponding data (including chromatographic peak retention times, peak areas, calculated concentrations, injection volumes, injection times, and sample identifi-

ers) for all analyses, and instrument logbook pages were submitted for review. The LESC data base manager reviewed the field and laboratory results, identified any data that appeared unusual, and reconciled the results prior to data base entry. All database entries were checked by a second person. Final hard copy and electronic results were accompanied by case narratives that described any problems or data interpretation difficulties, and associated corrective actions.

## Data Analysis

In addition to the computations described in the QA/QC section, comparisons of differences in mean %Rs for sample pairs were computed. The advantage of using paired samples (with the pairs being prepared and sampled under as nearly identical conditions as possible) is that the effect of uncertainty in the true concentrations of samples is reduced; also, accuracy comparisons thereby become insensitive to any possible differences in precision between the two methods being compared. The analyses were done mostly in terms of %Rs rather than actual measurements simply for ease of interpretation and comparison across different concentration levels and compounds. This approach was taken for the SPEW and transport study data, because of uncertainties in actual spiking concentrations. For TT samples, this approach was necessary because the true concentration of those samples was unknown and possibly varied with time.

For the purpose of obtaining approximate target concentrations to compute %Rs for TT samples, a weighted least-squares regression line was fit through the origin for SPEW samples for the AVOAS off-line and, separately, for EMSL-LV analyses. Mean measured concentrations were adjusted by the respective line to provide estimates of target concentrations for each port. These estimates were averaged when both AVOAS and EMSL-LV estimates were available. Measurements were converted to approximate %Rs so that results could be expressed on the same scale across different true concentration ranges and compounds. This conversion does not affect the precision results or the hypothesis tests of whether the mean recoveries are equal. The target concentration value is rough, and is used only for converting differences in mean measurements between measurement modes so as to approximate differences in mean %Rs.

**TABLE 2-6. INSTRUMENT COMPONENTS AND OPERATING CONDITIONS**

| Instrument | AVOAS System | EMSL-LV |
|---|---|---|
| Gas Chromatograph | SRI 8610 | HP 5890 Series 2 |
| Column | DB-624, 30-m (J&W) | RTX502.2, 105-m (Restek) |
| Carrier gas, flow rate | He, 6 cc/min | He, 10 cc/min |
| Oven temperature program | Initial 35°C<br>0.5 min 40°C<br>2.5 min 45°C<br>10.0 min 50°C<br>12.5 min 65°C | 45°C, 6°C/min to 143°C<br>(no hold time) |
| Purge and Trap Sampler | A⁺RT | OI 4460 with MPM-16 auto-sampler |
| Purge gas, flow rate | He, 12 cc/min | He, 40 cc/min |
| Purge time | 10 min | 11 min |
| Desorb time | 2 min | 2 min |
| Bake time | 8 min | 12 min |
| Trapping temperature | 30°C | 28°C |
| Desorb preheat | 180°C | 165°C |
| Desorb temperature | 215°C | 180°C |
| Bake temperature | 215°C | 180°C |
| Valve/transfer line temp. | 130°C | 80°C |
| Hall Detector | Tremetrics | OI Model 4420 |
| Reactor temperature | 885°C | 800°C |
| Reactor base temperature | 250°C | 240°C |
| Makeup gas, flow rate | He, 25 cc/min | He, 30 cc/min |
| Reaction gas, flow rate | $H_2$, 25 cc/min | $H_2$, 85 cc/min |
| n-Propanol flow | 60 μL/min | 50 μL/min |
| Photoionization Detector | Not used | OI Model 4330 |
| Intensity | — | 6 |
| mV Signal | — | 11.9 |
| Base temperature | — | 235°C |
| Integrator | Spectra-Physics 4400 | HP 3396 |
| Computer | IBM-Compatible 286 | IBM 286 PC |
| Software | A⁺RT | HP File server |

**TABLE 2-7. CHRONOLOGY OF AVOAS DEMONSTRATION ACTIVITIES**

| Predemonstration Activities | Date |
|---|---|
| Project planning, experimental design | March, 1991 |
| Preparation of Demonstration and QA Plans | April, 1991 |
| Performance Evaluation Study | April 12-15, 1991 |
| Preparation of ampoules of stock solutions for spiked purged effluent water samples at EMSL-LV | May 8, 1991 |
| Demonstration Activities | |
| Installation of AVOAS | May 14-17, 1991 |
| Preparation of purged effluent water at field site | May 16, 1991 |
| Demonstration:AVOAS analyses | May 18-24, 1991 |
| EMSL-LV Method 502.2 analyses | May 20-May 28, 1991 |
| Transport Study | May 30-June 13, 1991 |

The %Rs for each of the method pairs were computed for each day, and the mean values for each method over days were computed. The differences were assessed using paired-sample t-tests with a hypothesis of no difference in mean %Rs. Confidence intervals were also computed. For similar performance between two systems or treatments, one would expect a difference in mean %R of zero, with some allowance for random variability. The major advantage of paired comparison t-tests is their simplicity and ease of interpretation. In statistical terms, the paired-sample t-test amounts to blocking all other effects, and focusing only on the one effect of interest. Robustness is attained at the cost of degrees of freedom.

Paired-sample t-tests were used to assess all pairs of sample data. An Analysis of Variance (ANOVA) was used to evaluate TT sample data with respect to time of sample collection, day-to-day variability, mode of analysis (i.e., AVOAS on-line, AVOAS off-line, and Method 502.2), and sample port. An ANOVA models other effects which are either expected to be present or are possibly present and cannot be ruled out. In an ANOVA analysis, not all other effects which might be present are accommodated. On the other hand, if the model fitted for the other effects reasonably accommodates those that are in fact present, one obtains more degrees of freedom for error estimates, and hence better sensitivity (power). In addition, the ANOVA allows one to assess those other effects.

## AVOAS Demonstration Activities

A chronology of the activities and schedules for the AVOAS demonstration are included in Tables 2-7 and 2-8.

Activities prior to the demonstration included site reconnaissance, preparation of the Demonstration and QA Plans, the PE study, and preparation of spiking ampoules. Demonstration participants arrived at the Woburn field site on May 13. While the AVOAS was being installed, tested, and calibrated by A⁺RT, Inc., the EMSL-LV demonstration participants selected sample ports to be used for the demonstration, set up an area for preparing and shipping samples, and prepared and checked the PEW.

Daily activities at the field site during the demonstration included preparing SPEW, CCCS, and QCCS samples; collecting TT samples; preparing and shipping samples to EMSL-LV; entering and reviewing data; and analyzing the required AVOAS samples. Daily activities at the EMSL-LV laboratory included preparing QCCS and CCCS samples, receiving and logging in samples, performing the surrogate spikes, analyzing samples, and entering and reviewing data on the data spreadsheets.

Activities performed after the field portion of the demonstration included the transport study, data validation and verification, and data analysis and interpretation.

**TABLE 2-8. SCHEDULE OF SAMPLE ANALYSES FOR THE AVOAS AND EMSL-LV**

| AVOAS | | | | | |
|---|---|---|---|---|---|
| 5/18/91 | 5/20/91 | 15/21/91 | 5/22/91 | 5/23/91 | 5/24/91 |
| B (S6) | B (S6) | TTN (S4) | TTN (S4) | TTN (S3) | TTN (S3) |
| TTF (S3) | TTF (S4) | TTF (S4) | TTF (S4) | TTF (S3) | TTF (S3) |
| TTF (S3) | TTF(S4) | CCCS | CCCS | CCCS | CCCS |
| CCCS | CCCS | L | S | H | |
| L | S | M | L | M | TTN (S4) |
| H | H | H | M | S | TTF(S4) |
| S | M | S | H | L | L |
| M | L | QCCS | QCCS | QCCS | M |
| QCCS | QCCS | TTN (S3) | TTN (S3) | TTN (S4) | H |
| TTN (S4) | TTN (S3) | TTF(S3) | TTF (S3) | TTF (S4) | S |
| TTF (S4) | TTF (S3) | B (PEW) | B (PEW) | B (PEW) | QQCS |

| EMSL-LV | | | | | |
|---|---|---|---|---|---|
| 5/20/91 (Samples from 5/18/91) | 5/21/91 (Samples from 5/20/91) | 5/22/91 (Samples from 5/21/91) | 5/23/91 (Samples from 5/22/91) | 5/24/91 (Samples from 5/23/91) | 5/28/91 (Samples from 5/24/91) |
| B (Water) | B (Water) | B (Water) | B (Water) | Sur | Sur |
| CCCS | Recal* | CCCS | CCCS | CCCS | CCCS |
| B (PEW) | B (PEW) | B (PEW) | Sur | B (PEW) | B (PEW) |
| L | L | H | B (PEW) | L | L. |
| M | M | L | L | M (2) | M |
| H | H | M | M | H | M |
| S | S | S | H | S | S |
| TTA (3) | TTA (2) | TTA (2) | S | TTA (2) | TTA (2) |
| TTP (3) | TTP (2) | TTP (2) | TTA (2) | TTP (2) | TTP (2) |
| QCCS | B (PEW) | QCCS | TTP (2) | QCCS | QCCS |
| | QCCS | | QCCS | | QCCS |

| | | | |
|---|---|---|---|
| * | Recalibrated with 2, 20, 50, 100 ppb standards. | (S3): | Port S-3 sample. |
| B (S6): | VOC-free sample from port S6 (blank) | (S4): | Port S-4 sample. |
| B (PEW): | VOC-free purged effluent water (blank) | (2) or (3): | Number of sample replicates analyzed. |
| B (Water): | Reagent-grade water (blank) | H: | High spiked purged effluent water samples. |
| CCC: | Continuing calibration check standard. | L: | Low spiked purged effluent water samples. |
| QCCS: | Quality control check standard. | M: | Medium spiked purged effluent water samples. |
| Sur: | Reagent-grade water spiked with 2-bromo-1-chloropropane surrogate | S: | Superhigh spiked purged effluent water samples. |
| TTA: | Treatment train sample, a.m. | | |
| TTF: | Treatment train off-line sample (AVOAS). | | |
| TTN: | Treatment train on-line sample (AVOAS). | | |
| TTP: | Treatment train sample, p.m. | | |

# Section 3
## AVOAS Demonstration Results and Discussion

## Operational Results

The AVOAS demonstration went smoothly. Both the AVOAS and the EMSL-LV instruments were operational for the entire demonstration, and all of the samples specified in the Demonstration Plan were collected.

Initial installation and preliminary testing of the AVOAS took 2-1/2 days. The problems that occurred during installation were typical for an initial field site setup, and included delays and damages in shipping and the need to modify the site facilities (e.g., installing an air conditioner and vent).

During the ground-water treatment system pilot study of May 18 through May 30, 1991, the AVOAS processed 65 samples for the SITE demonstration (not including QC samples), 192 automated treatment system samples, 52 samples analyzed for another treatment project, and 41 calibration and blank samples. The AVOAS ran an average of 22.3 hours per day and processed an average of 24.4 samples per day, at an average run time of 55 min per sample. Further details of the AVOAS field performance, as reported by the developer, are included as Appendix A.

Deviations from the Demonstration Plan were minor, and their impact on the results is judged to be negligible. Modifications were made because of the large number of samples scheduled to be processed by the AVOAS during the same period, beyond those required for this demonstration. Deviations included:

1. Rescheduling the transport study until after the demonstration, with analysis of the transport study samples by EMSL-LV rather than by the field team.

2. Adjusting the planned sequence for sample analysis. Originally, the plan was to analyze the CCCS as the first sample of the day, and the QCCS as the last. The heavy analysis schedule for the SITE demonstration and for other

projects required modifying the sampling sequence so that the TT samples from port S-3 or S-4, which were analyzed last for routine monitoring purposes, would be the first samples for the AVOAS demonstration, analyzed as on-line TT samples.

3. Using the routine TT sample from port S-6 instead of a PEW sample as a system blank. This sample was used only if the S-6 sample was found to have target analyte concentrations <1.0 μg/L.

4. The AVOAS requires flushing of sample loops between analyses, and has a built-in mechanism for producing VOC-free water from TWP water for that purpose. However, at the demonstration site, the tap water contained a substance (possibly residual flux from new copper tubing) that caused a foaming problem. Bottled, purified water was used instead for flushing.

## Quantitative Results for Comparison Studies

### Comparison of the AVOAS and Method 502.2 Results for Treatment Train Samples

Tables 3-1(a-c) are compilations of results for TT samples analyzed by EMSL-LV and by the AVOAS in the on-line and off-line modes. Tables 3-2(a,b) summarize mean, standard deviation, and %RSD for EMSL-LV and AVOAS data by port and time.

Table 3-3 summarizes differences in mean %Rs for analytical mode comparisons for each of the three paired-analysis combinations (AVOAS on-line/AVOAS off-line; AVOAS off-line/EMSL-LV; AVOAS on-line/EMSL-LV) for samples from ports S-3 and S-4 and for both ports combined, over the demonstration period. Paired-sample t-tests of the hypothesis of no significant difference in mean %Rs were performed, and significance results are shown in Table 3-3.

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## TABLE 3-1(a). TREATMENT TRAIN SAMPLE RESULTS FOR EMSL-LV ANALYSES

| Compound | MDL (µg/L) | 1 a.m. S-3 | 1 p.m. S-4 | 2 a.m. S-4 | 2 p.m. S-3 | 3 a.m. S-4 | 3 p.m. S-3 | 4 a.m. S-4 | 4 p.m. S-3 | 5 a.m. S-3 | 5 p.m. S-4 | 6 a.m. S-3 | 6 p.m. S-4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,1-dichloroethene | 6.0 | 7.1 | 6.5 | U | U | U | U | U | 6.2 | 6.4 | U | 7.9 | 5.9* |
| trans-1,2-dichloroethene | 17.0 | U | U | U | U | U | U | U | U | U | U | U | U |
| 1,1-dichloroethane | 8.0 | U | U | U | U | U | U | U | U | U | U | U | U |
| cis-1,2-dichloroethene | 6.0 | 12.8 | U | 11.6 | 10.1 | 8.3 | 11.3 | 7.6 | 13.5 | 13.5 | 8.2 | 17.4 | 10.1 |
| 1,1,1-trichloroethane | 23.0 | 26.6 | 37.9 | 22.8* | 22.6* | 19.8* | 25.3 | 19.4* | 24.3 | 27.8 | 17.3* | 38.5 | 27.7 |
| trichloroethene | 22.0 | 53.1 | 49.3 | 50.3 | 49.3 | 41.4 | 50.2 | 42.9 | 54.9 | 56.1 | 39.4 | 73.1 | 45.3 |
| tetrachloroethene | 30.0 | 2042 | 2177 | 1882 | 2006 | 1915 | 1824 | 1837 | 2188 | 2204 | 2157 | 2133 | 2207 |

Detected Concentration, µg/L, for Demonstration Days 1 through 6

## TABLE 3-1(b). TREATMENT TRAIN SAMPLE RESULTS FOR THE AVOAS ON-LINE ANALYSES

| Compound | MDL (µg/L) | 1 a.m. S-3 | 1 p.m. S-4 | 2 a.m. S-4 | 2 p.m. S-3 | 3 a.m. S-4 | 3 p.m. S-3 | 4 a.m. S-4 | 4 p.m. S-3 | 5 a.m. S-3 | 5 p.m. S-4 | 6 a.m. S-3 | 6 p.m. S-4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,1-dichloroethene | 2.5 | 9.2 | 11.7 | 9.8 | 6.8 | 4.0 | 7.4 | 7.1 | 7.1 | 5.8 | 4.9 | 3.7 | 5.2 |
| trans-1,2-dichloroethene | 0.5 | U | 2.4 | U | 1.4 | U | 2.2 | U | 1.6 | U | 1.7 | U | 1.5 |
| 1,1-dichloroethane | 1.0 | 4.1 | 4.8 | 2.6 | 4.1 | 2.7 | 4.4 | 3.3 | 3.7 | 3.4 | 3.5 | 3.7 | 3.4 |
| cis-1,2-dichloroethene | 1.0 | 16.5 | 21.0 | 12.8 | 17.6 | 12.5 | 19.7 | 13.4 | 20.0 | 19.3 | 15.5 | 23.8 | 17.7 |
| 1,1,1-trichloroethane | 3.5 | 30.3 | 51.7 | 20.1 | 33.8 | 23.5 | 36.2 | 25.0 | 33.2 | 36.8 | 30.5 | 45.8 | 36.6 |
| trichloroethene | 1.5 | 56.3 | 82.6 | 48.1 | 64.3 | 46.6 | 74.4 | 50.1 | 72.6 | 77.3 | 63.0 | 95.1 | 72.3 |
| tetrachloroethene | 0.5 | 1924 | 2713 | 1986 | 2124 | 2058 | 2368 | 2249 | 2370 | 2366 | 2385 | 3030 | 2758 |

Detected Concentration, µg/L, for Demonstration Days 1 through 6

## TABLE 3-1(c). TREATMENT TRAIN SAMPLE RESULTS FOR THE AVOAS OFF-LINE ANALYSES

| Compound | MDL (µg/L) | 1 a.m. S-3 | 1 p.m. S-4 | 2 a.m. S-4 | 2 p.m. S-3 | 3 a.m. S-4 | 3 p.m. S-3 | 4 a.m. S-4 | 4 p.m. S-3 | 5 a.m. S-3 | 5 p.m. S-4 | 6 a.m. S-3 | 6 p.m. S-4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,1-dichloroethene | 2.5 | 7.3 | 9.1 | 5.0 | 5.3 | 3.2 | 6.9 | 5.3 | 6.4 | 3.1 | 5.3 | 3.3 | 6.1 |
| trans-1,2-dichloroethene | 0.5 | U | 1.7 | U | 1.3 | U | 1.5 | U | 0.9 | U | 1.7 | U | 1.1 |
| 1,1-dichloroethane | 1.0 | 4.2 | 3.8 | 2.6 | 3.8 | 2.6 | 4.2 | 3.0 | 3.5 | 3.2 | 3.2 | 3.7 | 3.8 |
| cis-1,2-dichloroethene | 1.0 | 16.7 | 15.7 | 12.2 | 17.8 | 11.8 | 20.5 | 12.9 | 18.5 | 17.6 | 14.7 | 23.1 | 16.3 |
| 1,1,1-trichloroethane | 3.5 | 35.0 | 39.2 | 26.4 | 35.7 | 25.3 | 37.4 | 25.8 | 36.4 | 39.8 | 32.3 | 45.5 | 36.3 |
| trichloroethene | 1.5 | 58.0 | 63.3 | 49.3 | 64.7 | 46.6 | 72.3 | 50.9 | 71.0 | 73.6 | 64.2 | 93.2 | 70.1 |
| tetrachloroethene | 0.5 | 1944 | 2406 | 2123 | 2195 | 2039 | 2365 | 2289 | 2391 | 2219 | 2278 | 2921 | 2806 |

Detected Concentration, µg/L, for Demonstration Days 1 through 6

*Vinyl chloride and 1,2-dichloroethane were not detected by either EMSL-LV or the AVOAS, so those compounds are not included in this table.*

MDL: Method Detection Limit

U: Below instrument detection limits.

*: Estimated value; measured concentration below calculated method detection limit.

Table 3-4 summarizes the results of analysis of variance (ANOVA) computations, performed to determine the significance of effects on the data attributable to port (S-3 or S-4); time of day (morning- or afternoon-collected samples); day-to-day differences over the demonstration period; and mode or analytical system differences (AVOAS on-line, AVOAS off-line, and EMSL-LV). Measured concentrations were used for the ANOVA computations. Results for each compound were computed separately for the EMSL-LV data, the AVOAS data, and for the AVOAS and EMSL-LV data combined.

## Mode Comparisons

*AVOAS On-line and Off-line Mode Comparisons* — For all compounds and ports, the measured concentrations were greater for on-line than for off-line measurements (except for 1,1,1-TCA). The difference in mean %R results indicated, however, that this difference was not significant or only slightly significant for most pairs. The difference in mean %R was greater for the two most volatile compounds (1,1-DCE and trans-1,2-DCE) than for the other compounds. It must be pointed out that the concentrations for the higher volatility compounds in the TT samples were very low (close to instrument detection limits) for 1,1-DCE, trans-1,2-DCE, and 1,1-DCA compared to the lower volatility compounds, particularly TCE and PCE, which had concentrations of around 65 µg/L and over 2300 µg/L, respectively. For TCE and PCE, the differences in mean %R between on-line and off-line sample analyses were very low (less than

**TABLE 3-2(a). SUMMARY OF MEAN, STANDARD DEVIATION, AND %RSD FOR PORT MEASUREMENTS FOR EMSL-LV, AVOAS ON-LINE, AND AVOAS OFF-LINE ANALYSES OF TREATMENT TRAIN SAMPLES ACROSS THE SIX DAYS OF THE DEMONSTRATION**

| | Port 3 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mean Concentration, µg/L | | | Standard Deviation | | | %RSD | | |
| Compound | EMSL-LV | AVOAS On-Line | AVOAS Off-line | EMSL-LV | AVOAS On-Line | AVOAS Off-line | EMSL-LV | AVOAS On-Line | AVOAS Off-line |
| 1,1-dichloroethene | [a] | 6.7 | 5.4 | — | 1.8 | 1.8 | — | 27.4 | 33.8 |
| trans-1,2-dichloroethene | U | [b] | [b] | — | [b] | [b] | — | [b] | [b] |
| 1,1-dichloroethane | U | 3.9 | 3.8 | — | 0.4 | 0.4 | — | 9.3 | 10.4 |
| cis-1,2-dichloroethene | 13.1 | 19.5 | 19.0 | 2.5 | 2.5 | 2.4 | 19.1 | 12.9 | 12.4 |
| 1,1,1-trichloroethane | 27.5 | 36.0 | 38.3 | 5.7 | 5.3 | 3.9 | 20.6 | 14.8 | 10.2 |
| trichloroethene | 56.1 | 73.3 | 72.1 | 8.7 | 13.1 | 11.9 | 15.5 | 17.9 | 16.4 |
| tetrachloroethene | 2066 | 2364 | 2339 | 142 | 373 | 323 | 6.9 | 15.8 | 14.0 |

| | Port 4 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mean Concentration, µg/L | | | Standard Deviation | | | %RSD | | |
| Compound | EMSL-LV | AVOAS On-Line | AVOAS Off-line | EMSL-LV | AVOAS On-Line | AVOAS Off-line | EMSL-LV | AVOAS On-Line | AVOAS Off-line |
| 1,1-dichloroethene | 6.2 | 7.1 | 5.7 | 0.4 | 3.0 | 1.9 | 6.8 | 42.9 | 34.2 |
| trans-1,2-dichloroethene | U | [b] | [b] | — | — | — | — | — | — |
| 1,1-dichloroethane | U | 3.4 | 3.2 | — | 0.8 | 0.5 | — | 23.3 | 17.1 |
| cis-1,2-dichloroethene | 9.2[c] | 15.5 | 13.3 | 1.7 | 3.3 | 1.9 | 18.0 | 21.6 | 13.6 |
| 1,1,1-trichloroethane | 24.2 | 31.2 | 30.9 | 7.6 | 11.6 | 6.0 | 31.6 | 37.1 | 19.3 |
| trichloroethene | 44.8 | 60.5 | 57.4 | 4.4 | 14.8 | 9.7 | 9.7 | 24.4 | 16.8 |
| tetrachloroethene | 2029 | 2358 | 2324 | 168 | 325 | 270 | 8.3 | 13.8 | 11.6 |

*U: Below instrument detection limits.*

[a] *Six of 12 values were "U"; no computations.*

[b] *Trans-1,2-dichloroethene was detected in p.m. samples only.*

[c] *Based on n=5, because one value was "U."*

**TABLE 3-2(b). SUMMARY OF MEAN, STANDARD DEVIATION, AND %RSD FOR SAMPLE TIME MEASURE-MENTS FOR EMSL-LV, AVOAS ON-LINE, AND AVOAS OFF-LINE (A.M. AND P.M.) ANALYSES OF TREATMENT TRAIN SAMPLES ACROSS THE SIX DAYS OF THE DEMONSTRATION**

| | A.M. - Collected Samples | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mean Concentration, µg/L | | | Standard Deviation | | | %RSD | | |
| Compound | EMSL-LV | On | Off | EMSL-LV | On | Off | EMSL-LV | On | Off |
| 1,1-dichloroethene | a | 6.6 | 4.3 | 0.8 | 2.6 | 1.7 | 10.5 | 39.0 | 36.7 |
| trans-1,2-dichloroethene | U | U[b] | U[b] | — | b | b | — | b | b |
| 1,1-dichloroethane | U | 3.3 | 3.2 | — | 0.6 | 0.6 | — | 17.4 | 19.7 |
| cis-1,2-dichloroethene | 11.9 | 16.4 | 15.7 | 3.6 | 4.5 | 4.4 | 30.4 | 27.3 | 27.7 |
| 1,1,1-trichloroethane | 25.8 | 30.3 | 33.0 | 7.1 | 9.6 | 8.5 | 27.5 | 31.7 | 25.8 |
| trichloroethene | 52.8 | 62.3 | 61.9 | 11.5 | 19.7 | 18.1 | 21.7 | 31.6 | 29.3 |
| tetrachloroethene | 2002 | 2269 | 2256 | 148 | 408 | 348 | 7.4 | 18.0 | 15.4 |

| | P.M. - Collected Samples | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mean Concentration, µg/L | | | Standard Deviation | | | %RSD | | |
| Compound | EMSL-LV | On | Off | EMSL-LV | On | Off | EMSL-LV | On | Off |
| 1,1-dichloroethene | 6.2 | 7.2 | 6.5 | 0.3 | 2.4 | 1.4 | 4.8 | 34.0 | 21.7 |
| trans-1,2-dichloroethene | U | 1.8 | 1.4 | — | 0.40 | 0.33 | — | 22.5 | 23.3 |
| 1,1-dichloroethane | U | 4.0 | 3.7 | — | 0.5 | 0.3 | — | 13.8 | 9.1 |
| cis-1,2-dichloroethene | 10.6[c] | 18.6 | 17.3 | 1.9[c] | 2.0 | 2.1 | 18.3[c] | 10.9 | 12.2 |
| 1,1,1-trichloroethane | 25.9 | 37.0 | 36.2 | 6.9 | 7.5 | 2.3 | 26.5 | 20.4 | 6.3 |
| trichloroethene | 48.1 | 71.5 | 67.6 | 5.2 | 7.2 | 4.0 | 10.9 | 10.0 | 5.9 |
| tetrachloroethene | 2093 | 2453 | 2407 | 150 | 240 | 211 | 7.2 | 9.8 | 8.8 |

U: Below instrument detection limits.

[a] Six of 12 values were "U"; no computations.

[b] Trans-12-dichloroethene was detected in p.m. samples only.

[c] Based on n=5, because one value was "U."

5% overall). The ANOVA results support the finding of no significant difference due to on-line or off-line modes, except for the high volatility, low concentration analytes 1,1-DCE and trans-1,2-DCE.

*AVOAS and EMSL-LV Comparisons* — The very high concentrations of PCE required sample dilution to bring PCE concentrations to within the linear range of the EMSL-LV detector. Sample dilution reduced the quantity of the lower concentration analytes (1,1-DCE, trans-1,2-DCE, 1,1-DCA, cis-1,2-DCE, and 1,2-DCA) to below the MDLs of the EMSL-LV instrument. Furthermore, the MDLs for the EMSL-LV instrument were somewhat higher than those for the AVOAS; i.e., the AVOAS instrument had greater sensitivity than the EMSL-LV instrument. For these reasons, the

AVOAS results indicate detectable concentrations of analytes for a number of samples for which concentrations were below the MDLs of the EMSL-LV detector.

For analytes detected by both instruments, virtually all of the AVOAS concentrations for both the on-line and off-line modes were higher than the EMSL-LV values, and all differences in mean %R, with the exception of 1,1-DCE and PCE for port S-3, were statistically significant at the 10% level. For the on-line AVOAS and EMSL-LV comparisons, the difference for TCE was approximately 21% for samples from both ports, and for PCE, approximately 12% for samples from both ports. The ANOVA results reinforce the finding of a significant effect due to analytical system. Figure 3-1

shows EMSL-LV and AVOAS on-line and off-line TT sample results, averaged over port and time of day.

*Sample Port Differences* — For all AVOAS on-line and off-line measurements, concentrations of all compounds measured for port S-3 samples, except for 1,1-DCE, were greater than those for port S-4 samples. The ANOVA results indicate that the differences were statistically significant for 1,1-DCA, cis-1,2-DCE, 1,1,1-TCA, and TCE. It is possible that these differences reflect actual differ-

**TABLE 3-3. DIFFERENCE IN MEAN PERCENT RECOVERIES FOR TREATMENT TRAIN SAMPLES ANALYZED BY THE AVOAS AND EMSL-LV.**

| Compound | On-line – Off-line AVOAS | | Off-line – EMSL-LV | | On-line – EMSL-LV | |
|---|---|---|---|---|---|---|
| | Port 3 | Port 4 | Port 3 | Port 4 | Port 3 | Port 4 |
| 1,1-dichloroethene[a] | 19 S | 25 NS | -3 NS | 27 S | 16 NS | 52 S |
| trans-1,2-dichloroethene[b] | 37 NS | 26 NS | c | c | c | c |
| 1,1-dichloroethane | 4 M | 6 NS | c | c | c | c |
| cis-1,2-dichloroethene | 2 NS | 12 M | 31 S | 45 S | 34 S | 57 S |
| 1,1,1-trichloroethane | -6 S | 1 NS | 29 S | 22 S | 23 S | 23 S |
| trichloroethene | 2 NS | 5 NS | 23 S | 21 S | 21 S | 26 S |
| tetrachloroethene | 1 NS | 1 NS | 11 M | 12 S | 12 M | 13 S |

*Vinyl chloride and 1,2-dichloroethane were not detected by either EMSL-LV or the AVOAS, so those compounds are not included in this table.*
[a] *For EMSL-LV, two of six samples for Port S-3 and four of six samples for Port S-4 had concentrations below instrument detection limits.*
[b] *All morning AVOAS measurements had concentrations below instrument detection limits.*
[c] *Compound not detected by EMSL-LV instrument; no computation possible.*
NS:  *Not significant (p > 0.10).*
M:   *Moderately significant (0.05 < p < 0.10)*
S:   *Significant (p < 0.05)*

**TABLE 3-4. SUMMARY OF ANALYSIS OF VARIANCE RESULTS FOR TREATMENT TRAIN SAMPLES**

| Compound | EMSL-LV | | | AVOAS | | | | AVOAS AND EMSL-LV | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Port | Time | Day | Port | Time | Day | Mode | Port | Time | Day | Mode |
| 1,1-dichloroethene | M | NS | M | NS | S | H | S | NS | NS | H | S |
| trans-1,2-dichloroethene | a | a | a | NS | H | NS | S | a | a | a | a |
| 1,1-dichloroethane | a | a | a | H | H | H | NS | a | a | a | a |
| cis-1,2-dichloroethene | S | NS | NS | H | S | S | NS | H | NS | S | H |
| 1,1,1-trichloroethane | NS | NS | NS | S | S | S | NS | H | M | H | H |
| trichloroethene | S | NS | NS | H | S | H | NS | H | NS | H | H |
| tetrachloroethene | NS | NS | NS | NS | S | H | NS | NS | S | H | H |

[a] *Compound not detected by EMSL-LV; no computation possible.*
Port:  *Port differences (S-3, S-4).*
Time:  *Time-of-day differences (a.m., p.m.).*
Day:   *Day-to-day differences (for the 6 days of the demonstration).*
Mode:  *Analytical system differences; does not apply to EMSL-LV analyses.  For the AVOAS, refers to differences between on-line and off-line measurements.*
NS:  *Not significant (p >0.10).*
M:   *Moderately significant (0.05 <p <0.10).*
S:   *Significant (0.01 <p <0.05).*
H:   *Highly significant (p <0.01).*

ences in water composition for samples from each port. However, for the EMSL-LV measurements, the significance of port among analytes was variable. The data are confounded by higher concentrations detected by the AVOAS in some afternoon collected/analyzed samples compared to morning samples.

*Time Differences* — No significant differences for time of sample collection were detected for any compound measured by the EMSL-LV instrument; however, for the AVOAS, time of collection/analysis effects were significant or highly significant for every compound. The results for the AVOAS afternoon analyses were always greater
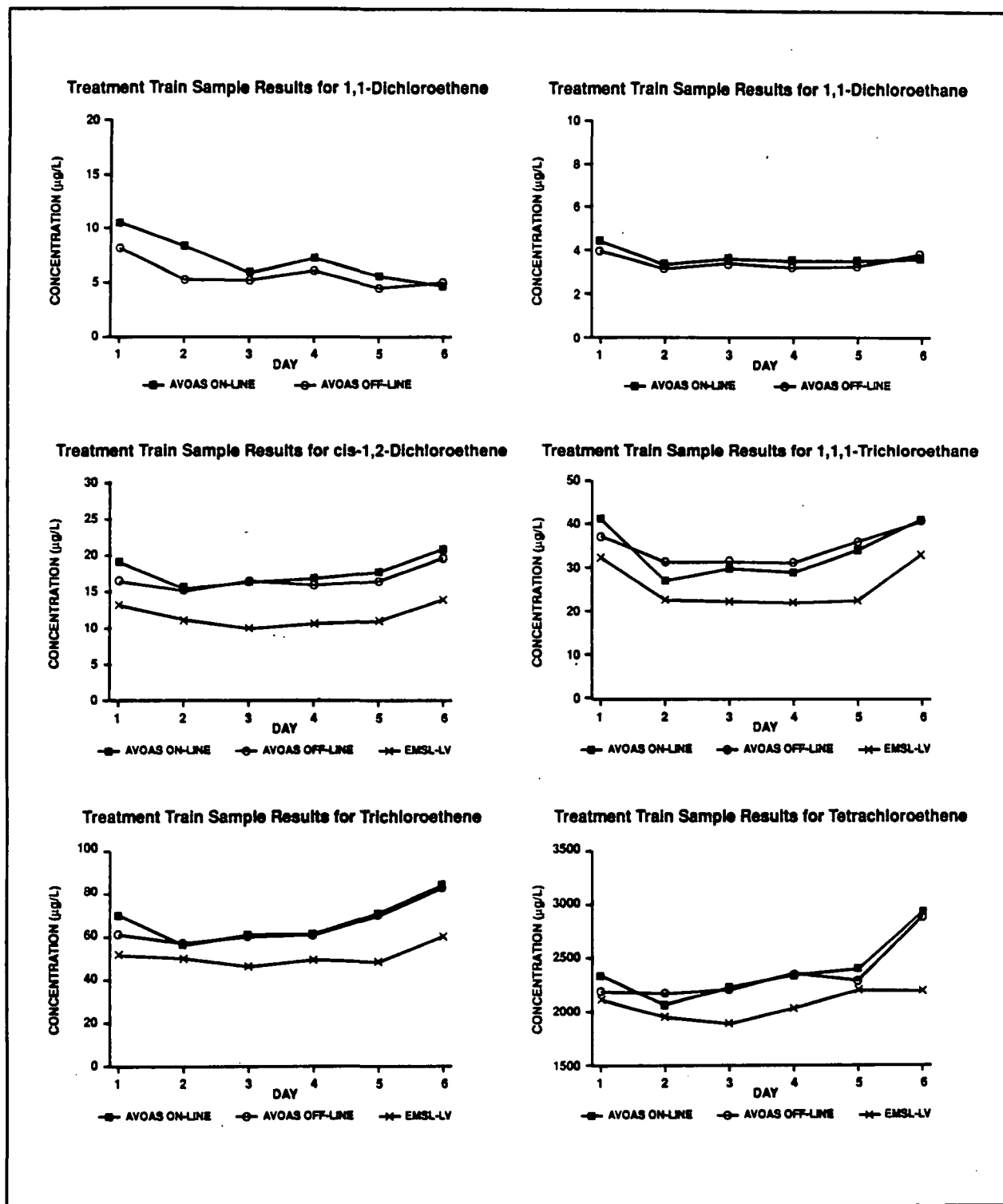


Figure 3-1. Treatment Train Sample Results. (Over all ports and times.)

than those for the morning analyses. For example, none of the morning AVOAS measurements contained detectable concentrations of trans-1,2-DCE, whereas all afternoon samples did. This finding is consistent with carryover from higher concentration samples analyzed between the morning and afternoon analyses. The superhigh-concentration SPEW samples were analyzed between the morning and afternoon TT analyses using the same loop as that used for the TT samples. The TT samples contained much lower concentrations of all analytes (except TCE and PCE) than the superhigh-concentration SPEW samples.

*Day-to-Day Differences* — For the EMSL-LV data, no significant differences in results from day to day were observed. For the AVOAS, day-to-day differences were statistically significant for all compounds but one (trans-1,2-DCE). Although the differences are significant, the magnitude is not great. Most values for TCE and PCE were within ± 30% of the 6-day mean concentrations. Possible explanations for this finding could include: 1) actual changes in treatment train water concentrations over the demonstration period; 2) factors intrinsic to the AVOAS, such as variations in instrument function over the demonstration period; or 3) random variability. The fact that the EMSL-LV measurements show no significant day-to-day difference suggests that variation in treatment train water over the 6-day period is not an explanation.

## Precision for Treatment Train Samples

Percent RSD values for both the AVOAS and EMSL-LV were less than 25%, except for 1,1-DCE for the AVOAS, which was 35% for the on-line mode and 33% for off-line. Precision results for the AVOAS in the off-line mode tended to be slightly better than those for the on-line mode, except for 1,1,1-TCA.

For EMSL-LV, the %RSDs for TCE and PCE were 18% and 7% for all data over the 6 days. For the AVOAS the corresponding %RSDs for TCE and PCE were 20% and 12% for the off-line mode and 22% and 14% for the on-line mode.

For all compounds except PCE, the %RSD values for port S-4 were the same or greater than those of port S-3.

### *Comparison of the AVOAS and Method 502.2 Results for Spiked Purged Effluent Water Samples*

Tables 3-5(a-d) are compilations of the SPEW sample results of the AVOAS and EMSL-LV analyses for each of the nine compounds at

each of the four concentration ranges. Table 3-6 summarizes data for differences in mean %Rs. The results of paired-sample t-tests of the hypothesis of no significant difference in mean %Rs between the AVOAS and EMSL-LV are included in that table. Plots of mean %Rs for both methods are shown in Figure 3-2.
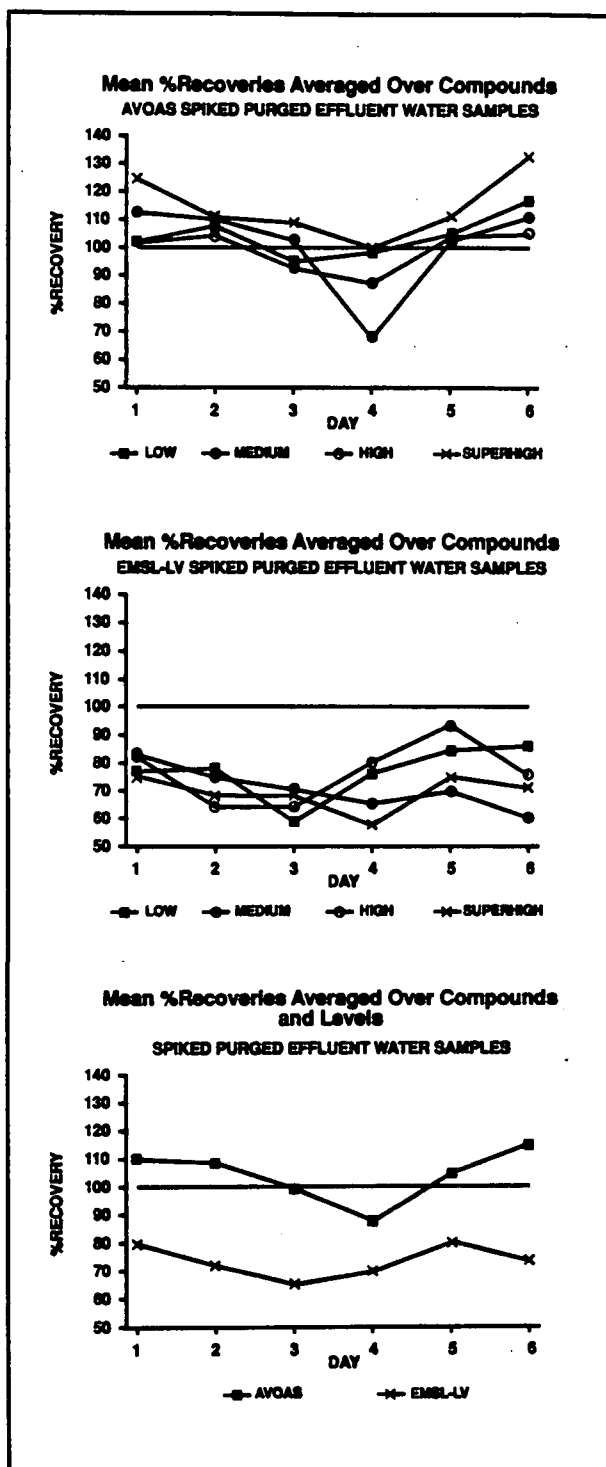


Figure 3-2. Spiked Purged Effluent Water Results.

In every case, the mean %R was greater for the AVOAS than for the corresponding EMSL-LV analysis. All but three of the differences were significant (p<0.05). For most analytes, the EMSL-LV measured concentrations were near or below the spiked target values; i.e., the %Rs were less than 100%, whereas the AVOAS results were usually close to or above the spiked values. The overall %R averaged over all compounds, days, and concentration levels for EMSL-LV was 74%; that

**TABLE 3-5(a). LOW-CONCENTRATION SPIKED PURGED EFFLUENT WATER SAMPLE RESULTS FOR EMSL-LV AND AVOAS ANALYSES**

| EMSL-LV | | Detected Concentration, µg/L, by Day | | | | | | Summary | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Target Conc. (µg/L) | 1 | 2 | 3 | 4 | 5 | 6 | Mean Conc. (µg/L) | Standard Deviation | %RSD | Mean %R |
| vinyl chloride | 22.4 | 20.8 | 20.1 | 10.7 | 20.6 | 21.6 | 20.2 | 19.0 | 4.1 | 21.6 | 85 |
| 1,1-dichloroethene | 4.6 | 4.0 | 4.0 | 2.8 | 3.9 | 4.2 | 5.0 | 4.0 | 0.7 | 17.7 | 87 |
| trans-1,2-dichloroethene | 13.8 | 9.9 | 9.9 | 7.4 | 9.8 | 10.3 | 9.8 | 9.5 | 1.1 | 11.1 | 69 |
| 1,1-dichloroethane | 9.1 | 6.5 | 6.7 | 5.1 | 6.5 | 7.0 | 6.7 | 6.4 | 0.7 | 10.5 | 70 |
| cis-1,2-dichloroethene | 28.1 | 21.5 | 21.5 | 17.2 | 20.9 | 22.9 | 20.9 | 20.8 | 1.9 | 9.2 | 74 |
| 1,1,1-trichloroethane | 9.1 | 5.6 | 6.5 | 5.1 | 6.1 | 7.1 | 11.2 | 6.9 | 2.2 | 31.8 | 76 |
| 1,2-dichloroethane | 9.0 | 7.1 | 6.9 | 6.1 | 6.8 | 7.8 | 6.7 | 6.9 | 0.6 | 8.0 | 76 |
| trichloroethene | 21.3 | 16.3 | 16.7 | 13.2 | 16.0 | 18.4 | 16.1 | 16.1 | 1.7 | 10.4 | 76 |
| tetrachloroethene | 23.7 | 19.0 | 19.4 | 15.3 | 18.0 | 20.8 | 19.7 | 18.7 | 1.9 | 10.2 | 79 |

| AVOAS | | Detected Concentration, µg/L, by Day | | | | | | Summary | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Target Conc. (µg/L) | 1 | 2 | 3 | 4 | 5 | 6 | Mean Conc. (µg/L) | Standard Deviation | %RSD | Mean %R |
| vinyl chloride | 22.4 | 32.6 | 36.8 | 28.0 | 30.3 | 31.6 | 32.0 | 31.9 | 2.9 | 9.1 | 142 |
| 1,1-dichloroethene | 4.6 | 4.5 | 4.5 | 3.8 | 4.3 | 4.2 | 4.5 | 4.3 | 0.3 | 6.5 | 94 |
| trans-1,2-dichloroethene | 13.8 | 13.3 | 13.6 | 12.0 | 10.2 | 10.8 | 13.6 | 12.2 | 1.5 | 12.2 | 89 |
| 1,1-dichloroethane | 9.1 | 9.2 | 9.5 | 8.7 | 8.7 | 9.5 | 9.7 | 9.2 | 0.4 | 4.8 | 101 |
| cis-1,2-dichloroethene | 28.1 | 27.1 | 28.4 | 26.3 | 27.5 | 30.0 | 27.3 | 27.8 | 1.3 | 4.6 | 99 |
| 1,1,1-trichloroethane | 9.1 | 8.7 | 9.5 | 8.6 | 9.5 | 10.4 | 17.3 | 10.7 | 3.3 | 31.0 | 117 |
| 1,2-dichloroethane | 9.0 | 8.8 | 8.8 | 8.4 | 8.9 | 9.6 | 9.3 | 9.0 | 0.4 | 4.5 | 99 |
| trichloroethene | 21.3 | 20.5 | 22.2 | 19.6 | 19.9 | 21.5 | 22.5 | 21.0 | 1.2 | 5.7 | 99 |
| tetrachloroethene | 23.7 | 21.8 | 23.3 | 21.1 | 21.5 | 22.1 | 24.8 | 22.4 | 1.4 | 6.2 | 95 |

*Target Conc.: Concentration of spiking solution.*
*Mean Conc.: Mean concentration over 6 days.*
*The standard deviation listed is for the measured concentrations (not for the %Rs).*
*%RSD:  Percent relative standard deviation.*
*Mean %R:  Mean percent recovery.*

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for the AVOAS was 104%. Possible explanations for these findings include: 1) differences in performance of the instruments, 2) variability in analyst technique, or 3) transport or holding time effects. The data indicate that a combination of these sources may have contributed to the observed results.

The day-to-day patterns for the AVOAS and EMSL-LV are similar, though not identical. Some exceptions can be noted. For example, the AVOAS results for the medium-concentration SPEW sample for day 4 had markedly lower concentrations of all analytes compared to the other days and to those for the EMSL-LV instrument; for day 3, the

### TABLE 3-5(b). MEDIUM-CONCENTRATION SPIKED PURGED EFFLUENT WATER SAMPLE RESULTS FOR EMSL-LV AND AVOAS ANALYSES

| EMSL-LV | | Detected Concentration, µg/L, by Day | | | | | | Summary | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Target Conc. (µg/L) | 1 | 2 | 3 | 4 | 5 | 6 | Mean Conc. (µg/L) | Standard Deviation | %RSD | Mean %R |
| vinyl chloride | 37.4 | 38.9 | 29.5 | 26.2 | 28.0 | 33.9 | 27.0 | 30.6 | 4.9 | 16.0 | 82 |
| 1,1-dichloroethene | 91.1 | 67.0 | 55.0 | 53.0 | 48.9 | 58.0 | 44.3 | 54.4 | 7.8 | 14.4 | 60 |
| trans-1,2-dichloroethene | 97.5 | 76.0 | 66.0 | 62.0 | 57.0 | 61.0 | 52.0 | 62.3 | 8.2 | 13.2 | 64 |
| 1,1-dichloroethane | 45.6 | 39.4 | 38.2 | 36.0 | 32.9 | 34.5 | 29.4 | 35.1 | 3.6 | 10.4 | 77 |
| cis-1,2-dichloroethene | 23.7 | 20.5 | 19.2 | 17.9 | 16.2 | 16.7 | 14.2 | 17.5 | 2.2 | 12.9 | 74 |
| 1,1,1-trichloroethane | 91.1 | 74.0 | 67.0 | 62.0 | 58.0 | 62.0 | 60.0 | 63.8 | 5.8 | 9.1 | 70 |
| 1,2-dichloroethane | 39.2 | 33.1 | 33.6 | 32.2 | 28.9 | 28.1 | 26.9 | 30.5 | 2.8 | 9.3 | 78 |
| trichloroethene | 53.8 | 40.5 | 40.6 | 38.2 | 34.6 | 35.3 | 30.0 | 36.5 | 4.1 | 11.2 | 68 |
| tetrachloroethene | 88.7 | 75.0 | 66.0 | 63.0 | 55.0 | 56.0 | 46.8 | 60.3 | 9.8 | 16.3 | 68 |
| AVOAS | | Detected Concentration, µg/L, by Day | | | | | | Summary | | | |
| Compound | Target Conc. (µg/L) | 1 | 2 | 3 | 4 | 5 | 6 | Mean Conc. (µg/L) | Standard Deviation | %RSD | Mean %R |
| vinyl chloride | 37.4 | 60.2 | 56.6 | 51.8 | 34.7 | 54.5 | 58.0 | 52.6 | 9.2 | 17.6 | 141 |
| 1,1-dichloroethene | 91.1 | 75.0 | 72.0 | 67.8 | 43.2 | 71.1 | 70.1 | 66.5 | 11.7 | 17.6 | 73 |
| trans-1,2-dichloroethene | 97.5 | 98.1 | 99.6 | 90.9 | 60.5 | 71.1 | 97.2 | 86.2 | 16.4 | 19.1 | 88 |
| 1,1-dichloroethane | 45.6 | 55.8 | 53.6 | 52.2 | 34.4 | 53.3 | 55.0 | 50.7 | 8.1 | 16.0 | 111 |
| cis-1,2-dichloroethene | 23.7 | 25.5 | 25.1 | 23.2 | 15.1 | 23.5 | 24.0 | 22.7 | 3.8 | 16.8 | 96 |
| 1,1,1-trichloroethane | 91.1 | 110 | 108 | 104 | 62.9 | 97.4 | 112 | 98.9 | 18.4 | 18.6 | 109 |
| 1,2-dichloroethane | 39.2 | 45.5 | 42.4 | 40.0 | 28.0 | 43.6 | 42.6 | 40.4 | 6.3 | 15.6 | 103 |
| trichloroethene | 53.8 | 56.5 | 57.2 | 51.1 | 34.1 | 51.9 | 55.6 | 51.1 | 8.7 | 17.0 | 95 |
| tetrachloroethene | 88.7 | 88.6 | 89.8 | 82.3 | 52.2 | 80.2 | 91.3 | 80.7 | 14.6 | 18.1 | 91 |

Target Conc.: Concentration of spiking solution.
Mean Conc.: Mean concentration over 6 days.
The standard deviation listed is for the measured concentrations (not for the %Rs).
%RSD: Percent relative standard deviation.
Mean %R: Mean percent recovery.

EMSL-LV analyses of the low-concentration SPEW samples had markedly lower concentrations for all components than on the other days.

Precision for the AVOAS and for the EMSL-LV instruments for the combined values across all concentrations and compounds was similar (12.8 and 13.0%). Results for all four concentration ranges were <30 %RSD for both the AVOAS and the EMSL-LV data, with the exception of 1,1,1-TCA in the low-concentration samples. The higher (31 to 32%) RSD for the 1,1,1-TCA replicates was

**TABLE 3-5(c). HIGH-CONCENTRATION SPIKED PURGED EFFLUENT WATER SAMPLE RESULTS FOR EMSL-LV AND AVOAS ANALYSES**

| EMSL-LV | | Detected Concentration, µg/L, by Day | | | | | | Summary | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Target Conc. (µg/L) | 1 | 2 | 3 | 4 | 5 | 6 | Mean Conc. (µg/L) | Standard Deviation | %RSD | Mean %R |
| vinyl chloride | 224 | 243 | 157 | 173 | 236 | 274 | 237 | 219 | 44.8 | 20.4 | 98 |
| 1,1-dichloroethene | 45.6 | 42.0 | 30.2 | 32.7 | 40.2 | 47.2 | 38.7 | 38.5 | 6.2 | 16.2 | 84 |
| trans-1,2-dichloroethene | 138 | 105 | 79.0 | 82.0 | 102 | 124 | 96.0 | 98.0 | 16.5 | 16.8 | 71 |
| 1,1-dichloroethane | 91.1 | 68.0 | 54.0 | 55.0 | 69.0 | 81.0 | 62.0 | 64.8 | 10.1 | 15.6 | 71 |
| cis-1,2-dichloroethene | 281 | 223 | 169 | 174 | 214 | 245 | 192 | 203 | 29.7 | 14.6 | 72 |
| 1,1,1-trichloroethane | 91.1 | 61.0 | 62.0 | 53.0 | 65.0 | 86.0 | 69.0 | 66.0 | 11.1 | 16.9 | 72 |
| 1,2-dichloroethane | 90.2 | 73.0 | 60.0 | 57.0 | 72.0 | 79.0 | 66.0 | 67.8 | 8.4 | 12.3 | 75 |
| trichloroethene | 213 | 172 | 142 | 136 | 159 | 187 | 149 | 158 | 19.3 | 12.2 | 74 |
| tetrachloroethene | 237 | 198 | 158 | 153 | 180 | 204 | 162 | 176 | 21.6 | 12.3 | 74 |

| AVOAS | | Detected Concentration, µg/L, by Day | | | | | | Summary | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Target Conc. (µg/L) | 1 | 2 | 3 | 4 | 5 | 6 | Mean Conc. (µg/L) | Standard Deviation | %RSD | Mean %R |
| vinyl chloride | 224 | 332 | 356 | 269 | 297 | 301 | 310 | 311 | 30.4 | 9.8 | 139 |
| 1,1-dichloroethene | 45.6 | 44.6 | 46.1 | 39.8 | 40.9 | 47.0 | 47.3 | 44.3 | 3.2 | 7.2 | 97 |
| trans-1,2-dichloroethene | 138 | 132 | 135 | 118 | 114 | 103 | 135 | 123 | 13.2 | 10.8 | 89 |
| 1,1-dichloroethane | 91.1 | 90.0 | 89.8 | 83.7 | 80.6 | 93.5 | 90.1 | 87.9 | 4.8 | 5.4 | 97 |
| cis-1,2-dichloroethene | 281 | 267 | 270 | 248 | 217 | 285 | 265 | 259 | 23.6 | 9.1 | 92 |
| 1,1,1-trichloroethane | 91.1 | 86.0 | 87.5 | 81.5 | 69.0 | 101 | 89.1 | 85.6 | 10.3 | 12.0 | 94 |
| 1,2-dichloroethane | 90.2 | 86.1 | 82.6 | 79.6 | 68.9 | 92.9 | 89.3 | 83.2 | 8.5 | 10.2 | 92 |
| trichloroethene | 213 | 208 | 217 | 198 | 171 | 220 | 222 | 206 | 19.4 | 9.4 | 97 |
| tetrachloroethene | 237 | 228 | 233 | 216 | 189 | 234 | 251 | 225 | 21.0 | 9.3 | 95 |

*Target Conc.:* Concentration of spiking solution.
*Mean Conc.:* Mean concentration over 6 days.
The standard deviation listed is for the measured concentrations (not for the %Rs).
*%RSD:* Percent relative standard deviation.
*Mean %R:* Mean percent recovery.

a consequence of an exceptionally high concentration of this compound in the sample analyzed at both locations on the last day of the demonstration. It is possible that 1,1,1-TCA or a coeluting contaminant (i.e., a compound with a chromatographic retention time close to that of 1,1,1-TCA) was introduced into the samples at the site during SPEW sample preparation. The average precision for the AVOAS across all concentrations and compounds was 12.6 %RSD; that for EMSL-LV was 13.3%. This difference is so small as to be of no practical significance.

**TABLE 3-5(d). SUPERHIGH-CONCENTRATION SPIKED PURGED EFFLUENT WATER SAMPLE RESULTS FOR EMSL-LV AND AVOAS ANALYSES**

| EMSL-LV | | Detected Concentration, µg/L, by Day | | | | | | Summary | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Target Conc. (µg/L) | 1 | 2 | 3 | 4 | 5 | 6 | Mean Conc. (µg/L) | Standard Deviation | %RSD | Mean %R |
| vinyl chloride | 747 | 580 | 510 | 580 | 450 | 730 | 630 | 580 | 96.7 | 16.7 | 78 |
| 1,1-dichloroethene | — | — | — | — | — | — | — | — | — | — | — |
| trans-1,2-dichloroethene | 1946 | 1330 | 1240 | 1170 | 970 | 1340 | 1210 | 1210 | 135 | 11.2 | 62 |
| 1,1-dichloroethane | 911 | 720 | 680 | 620 | 540 | 700 | 720 | 663 | 70.9 | 10.7 | 73 |
| cis-1,2-dichloroethene | 467 | 345 | 305 | 286 | 261 | 306 | 329 | 305 | 29.9 | 9.8 | 65 |
| 1,1,1-trichloroethane | 1822 | 1280 | 1270 | 1310 | 1080 | 1380 | 1280 | 1267 | 99.9 | 7.9 | 70 |
| 1,2-dichloroethane | 788 | 650 | 580 | 530 | 493 | 570 | 550 | 562 | 53 | 9.4 | 71 |
| trichloroethene | 1067 | 810 | 730 | 690 | 590 | 750 | 720 | 715 | 73.1 | 10.2 | 67 |
| tetrachloroethene | 1774 | 1460 | 1240 | 1390 | 1020 · 1310 | 1200 | | 1270 | 155 | 12.2 | 72 |
| **AVOAS** | | Detected Concentration, µg/L, by Day | | | | | | Summary | | | |
| Compound | Target Conc. (µg/L) | 1 | 2 | 3 | 4 | 5 | 6 | Mean Conc. (µg/L) | Standard Deviation | %RSD | Mean %R |
| vinyl chloride | 747 | 1211 | 1038 | 1131 | 930 | 1218 | 1415 | 1157 | 167 | 14.4 | 155 |
| 1,1-dichloroethene | — | — | — | — | — | — | — | — | — | — | — |
| trans-1,2-dichloroethene | 1946 | 2024 | 1954 | 1823 | 1754 | 1897 | 2114 | 1928 | 132 | 6.8 | 99 |
| 1,1-dichloroethane | 911 | 1109 | 969 | 949 | 881 | 945 | 1111 | 994 | 94.6 | 9.5 | 109 |
| cis-1,2-dichloroethene | 467 | 547 | 489 | 456 | 430 | 463 | 535 | 487 | 46.3 | 9.5 | 104 |
| 1,1,1-trichloroethane | 1822 | 2368 | 1861 | 1946 | 1667 | 1973 | 2494 | 2053 | 313 | 15.2 | 112 |
| 1,2-dichloroethane | 788 | 899 | 784 | 788 | 687 | 747 | 955 | 810 | 99.1 | 12.2 | 103 |
| trichloroethene | 1067 | 1277 | 1220 | 1127 | 1071 | 1121 | 1324 | 1190 | 99.2 | 8.3 | 112 |
| tetrachloroethene | 1774 | 2227 | 2129 | 1929 | 1958 | 1935 | 2450 | 2150 | 208 | 9.9 | 119 |

Target Conc.: Concentration of spiking solution.
Mean Conc.: Mean concentration over 6 days.
The standard deviation listed is for the measured concentrations (not for the %Rs).
%RSD:      Percent relative standard deviation.
Mean %R:   Mean percent recovery.

**TABLE 3-6. DIFFERENCE IN MEAN PERCENT RECOVERIES FOR SPIKED PURGED EFFLUENT WATER SAMPLES ANALYZED BY THE AVOAS (OFF-LINE) AND EMSL-LV[a]**

| | Low Spike | Medium Spike | High Spike | Superhigh Spike | Mean, All |
|---|---|---|---|---|---|
| vinyl chloride | 58 | 59 | 40 | 77 | 59 |
| 1,1-dichloroethene | 6 NS | 13 | 13 M | [b] | 11 |
| trans-1,2-dichloroethene | 20 | 25 | 18 M | 37 | 25 |
| 1,1-dichloroethane | 31 | 34 | 25 | 36 | 32 |
| cis-1,2-dichloroethene | 25 | 22 | 20 | 39 | 26 |
| 1,1,1-trichloroethane | 41 | 39 | 22 | 43 | 36 |
| 1,2-dichloroethane | 23 | 25 | 17 | 31 | 24 |
| trichloroethene | 23 | 27 | 23 | 45 | 29 |
| tetrachloroethene | 16 | 23 | 21 | 47 | 27 |

[a] All values significantly different, except as noted ($p < 0.05$).

[b] 1,1-dichloroethene not in superhigh-concentration sample.

NS: Not significantly different ($p > 0.10$).

M: Moderately significant ($0.05 < p < 0.10$).

## Transport Study Results

Tables 3-7(a,b) and 3-8(a,b) are compilations of measured results for medium- and high-concentration spiked samples for the transport study. Paired-sample t-tests of the hypothesis of no significant difference in mean %R between nontransported and transported samples were performed. None of the individual paired-sample t-tests produced a significant result. However, concentrations for nontransported samples were greater than those for transported samples for 15 of the 18 pairs. This result would be highly statistically significant

if the various tests and analyses were statistically independent, but since they were not, we can only conclude that the data suggest that a transport effect may exist. The magnitude of the transport effect is not great, with the largest difference in mean %R approximately 23% for vinyl chloride (VC), the most volatile analyte. Twelve of the 18 differences in mean %R are less than 8%. Because of the small number of observations, all of the estimates have rather wide confidence intervals. Figure 3-3(a,b) shows transport study results for medium- and high-concentration spiked samples for TCE and PCE.
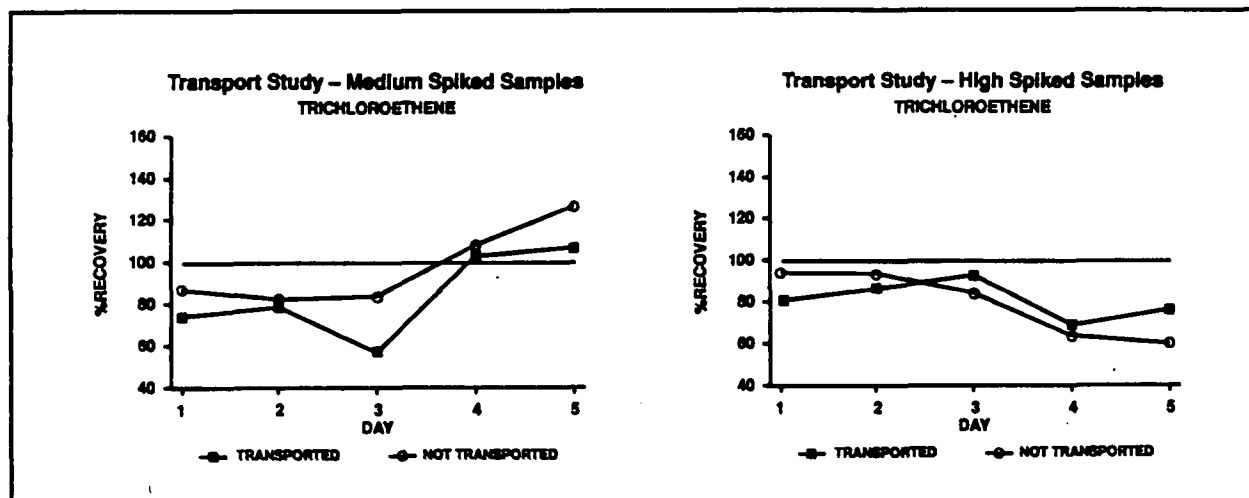


**Figure 3-3a. Transport Study Results for Medium- and High-concentration Spiked Samples for Trichloroethene.**
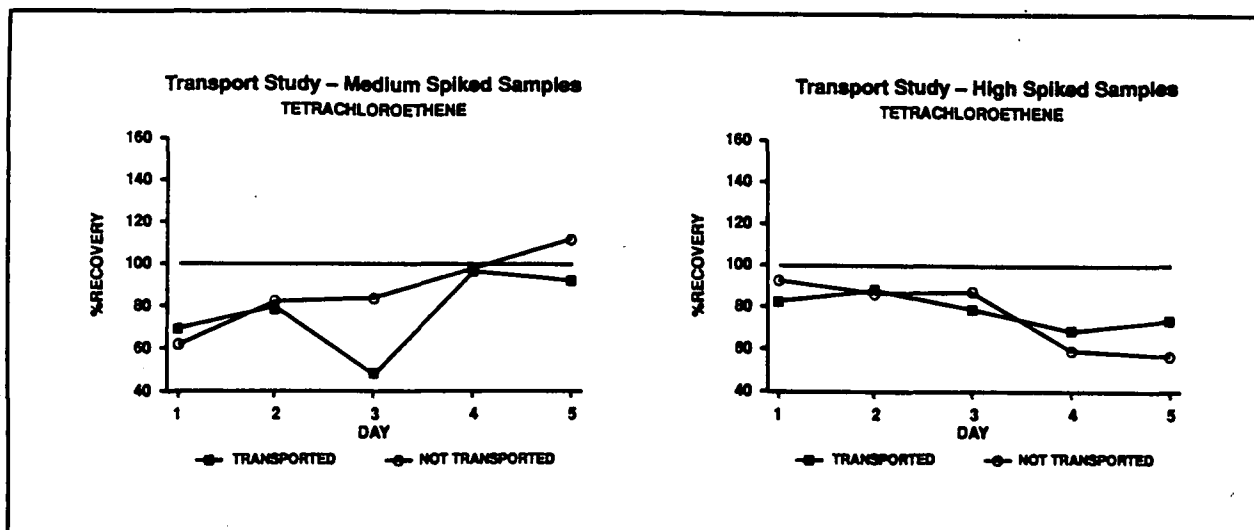
**Figure 3-3b. Transport Study Results for Medium- and High-concentration Spiked Samples for Tetrachloroethene.**

### TABLE 3-7(a). TRANSPORT STUDY RESULTS FOR MEDIUM SPIKED SAMPLES[a]

| | | Detected Concentration, µg/L, by Sample | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | | 2 | | 3 | | 4 | | 5 | |
| Compound | Target Conc. (µg/L) | Trans | Not Trans[b] | Trans | Not Trans | Trans | Not Trans | Trans | Not Trans | Trans | Not Trans |
| vinyl chloride | 37.4 | 36.5 | 35.5 | 47.9 | 36.3 | 35.8 | 55.0 | 103 | 84.1 | 80.6 | 93 |
| | | 36.6 | — | 38.3 | 51.0 | 54.0 | 44.2 | 86.1 | 92.5 | 81.7 | 127 |
| 1,1-dichloroethene | 91.1 | 61.0 | 53.0 | 74.0 | 70.0 | 60.0 | 82.0 | 97.6 | 93.5 | 92.3 | 102 |
| | | 61.0 | — | 61.0 | 75.0 | 99.0 | 66.0 | 98.6 | 102 | 94.1 | 130 |
| trans-1,2-dichloroethene | 97.5 | 68.0 | 60.0 | 81.0 | 78.0 | 39.4 | 97.0 | 94.1 | 91.9 | 98.2 | 99.5 |
| | | 68.0 | — | 68.0 | 80.0 | 50.0 | 70.0 | 95.4 | 105 | 91.6 | 128 |
| 1,1-dichloroethane | 45.6 | 39.2 | 33.8 | 46.4 | 41.6 | 26.1 | 47.3 | 53.3 | 51.6 | 59.4 | 56.8 |
| | | 38.4 | — | 38.5 | 43.1 | 30.5 | 38.6 | 52.2 | 56.2 | 51.8 | 78.4 |
| cis-1,2-dichloroethene | 23.7 | 19.4 | 16.2 | 22.2 | 21.9 | 17.3 | 24.9 | 25.5 | 26.1 | 28.6 | 27.1 |
| | | 18.8 | — | 18.8 | 20.8 | 20.8 | 18.9 | 29.5 | 26.3 | 24.8 | 36.3 |
| 1,1,1-trichloroethane | 91.1 | 66.0 | 60.0 | 80.0 | 48.4 | 34.3 | 56.0 | 89.7 | 95.8 | 103 | 99.6 |
| | | 65.0 | — | 64.0 | 70.0 | 38.7 | 65.0 | 101 | 89.6 | 87.7 | 127 |
| 1,2-dichloroethane | 39.2 | 33.5 | 31.7 | 36.8 | 35.8 | 25.2 | 37.6 | 41.9 | 44.9 | 46.1 | 44.6 |
| | | 33.3 | — | 32.8 | 36.0 | 27.6 | 31.6 | 47.7 | 42.5 | 23.8 | 61.5 |
| trichloroethene | 53.8 | 40.9 | 34.1 | 46.9 | 42.3 | 27.6 | 50.0 | 56.0 | 59.4 | 62.5 | 57.7 |
| | | 39.7 | — | 38.5 | 46.8 | 33.3 | 39.7 | 54.7 | 56.1 | 51.9 | 77.4 |
| tetrachloroethene | 88.7 | 65.0 | 54.0 | 76.0 | 67.0 | 37.6 | 86.0 | 81.9 | 87.4 | 80.3 | 86.9 |
| | | 57.0 | — | 63.0 | 79.0 | 45.9 | 63.0 | 87.2 | 84.7 | 80.9 | 110 |

[a] Results for duplicate samples for each treatment.
[b] Duplicate sample not analyzed.
Trans: sample transported.
Not trans: sample not transported.

**TABLE 3-7(b). SUMMARY OF TRANSPORT STUDY RESULTS FOR MEDIUM SPIKED SAMPLES**

| Compound | Mean Concentration | | Standard Deviation | | %RSD | | Mean %R | | Difference in Mean %R |
|---|---|---|---|---|---|---|---|---|---|
| | Trans | Not Trans | Trans | Not Trans | Trans | Not Trans | Trans | Not Trans | |
| vinyl chloride | 59.8 | 68.7 | 25.3 | 31.7 | 42.1 | 46.1 | 160.6 | 183.8 | 23.2 |
| 1,1-dichloroethene | 79.9 | 85.9 | 17.9 | 23.4 | 22.4 | 27.2 | 87.7 | 94.3 | 6.7 |
| trans-1,2-dichloroethene | 75.4 | 89.9 | 20.2 | 20.5 | 26.8 | 22.8 | 77.3 | 92.2 | 14.9 |
| 1,1-dichloroethane | 43.6 | 49.7 | 10.8 | 13.3 | 24.7 | 26.7 | 95.6 | 109.0 | 13.4 |
| cis-1,2-dichloroethene | 22.6 | 24.3 | 4.3 | 5.8 | 19.1 | 24.0 | 96.4 | 103.8 | 7.2 |
| 1,1,1-trichloroethane | 72.9 | 79.0 | 23.8 | 25.6 | 32.6 | 32.3 | 80.1 | 86.8 | 6.7 |
| 1,2-dichloroethane | 34.9 | 40.7 | 8.3 | 9.3 | 23.8 | 22.8 | 89.0 | 103.8 | 14.8 |
| trichloroethene | 45.2 | 51.5 | 11.1 | 13.0 | 24.4 | 25.2 | 84.0 | 96.6 | 11.7 |
| tetrachloroethene | 67.5 | 79.8 | 16.7 | 16.6 | 24.7 | 20.8 | 76.1 | 89.9 | 13.9 |

*Mean Concentration: Mean concentration for duplicate samples for five sample pairs.*
*%RSD:                        Percent relative standard deviation.*
*Mean %R:                  Mean percent recovery for duplicate samples for five sample pairs.*
*Difference in mean %R:  Difference in mean percent recovery between samples not transported and those transported.*

Several instances for which transport effects may have influenced the results can be observed. The estimated loss in TCE concentration for the medium-range transported sample was approximately 12%. However, the 90% confidence interval expands the potential loss to approximately 28%, which is consistent with the results for the AVOAS and EMSL-LV differences in mean %R for SPEW samples.

Most of the %Rs for both transported and nontransported samples, at both concentration ranges, were less than 100%. It is impossible to attribute with certainty a cause for these results; however, explanations could include: 1) analyte concentrations in the standards were less than the certified amounts, and 2) chemist spiking or analytical technique. For the SPEW samples, EMSL-LV %Rs also tended to be <100%. However, the %Rs of the SPEW samples analyzed by the AVOAS were close to 100%. The transport study samples were made using the same spiking solutions as those for the SPEW samples. In contrast, the QCCS samples, which were prepared at the respective locations, had %Rs close to 100% for both the AVOAS and EMSL-LV. The stock solution used to make the QCCSs was not the same as that used for the SPEW samples.

The results suggest that inter-analyst variability was significant; that is, the difference in recoveries obtained by the two chemists was larger in magnitude than any transport effect. This inter-analyst variability occurred despite the fact that each analyst had recalibrated the instrument before their respective days on the study. The analyst variability seems to differ for the medium- and high-concentration spikes. One explanation may be the difference in dilution techniques used by the analysts for the high-concentration samples. However, wide confidence intervals for each of the spiking concentrations preclude definitive conclusions. The analyst-to-analyst difference is similar in magnitude to the AVOAS - EMSL-LV differences found in the TT and SPEW sample comparisons, leading one to speculate whether the real differences between the AVOAS and EMSL-LV mean %Rs are due to transport phenomena, differences between instruments, differences between analysts, or a combination of these or other factors.

## Linearity Study Results

Data for off-line analyses of the SPEW samples were used to check the linearity of response of the AVOAS. The results suggest little evidence for nonlinearity for most of the target analytes at most

## TABLE 3-8(a). TRANSPORT STUDY RESULTS FOR HIGH SPIKED SAMPLES

| | | Detected Concentration, µg/L, by Sample | | | | | | | | | |
| | | 1 | | 2 | | 3 | | 4 | | 5 | |
| Compound | Target Conc. | Trans | Not Trans | Trans | Not Trans | Trans | Not Trans | Trans | Not Trans | Trans | Not Trans |
|---|---|---|---|---|---|---|---|---|---|---|---|
| vinyl chloride | 227 | 282 | 255 | 265 | 301 | 331 | 355 | 341 | 301 | 350 | 322 |
| | | 252 | 295 | 234 | 249 | 358 | 311 | 303 | 328 | 323 | 288 |
| 1,1-dichloroethene | 45.6 | 46.9 | 43.2 | 47.8 | 54.0 | 56.0 | 59.0 | 44.7 | 41.6 | 45.2 | 42.6 |
| | | 42.7 | 48.0 | 51.0 | 53.0 | 55.0 | 50.0 | 41.6 | 49.9 | 45.1 | 37.8 |
| trans-1,2-dichloroethene | 138 | 116 | 121 | 121 | 128 | 121 | 137 | 96.3 | 82.7 | 103 | 93.2 |
| | | 107 | 122 | 118 | 124 | 124 | 120 | 89.9 | 99.6 | 97.5 | 78.7 |
| 1,1-dichloroethane | 91.1 | 76.0 | 81.0 | 76.0 | 78.0 | 76.0 | 85.0 | 61.4 | 53.7 | 66.9 | 60.9 |
| | | 71.0 | 79.0 | 70.0 | 78.0 | 78.0 | 77.0 | 58.1 | 63.0 | 61.9 | 50.6 |
| cis-1,2-dichloroethene | 281 | 235 | 237 | 235 | 250 | 214 | 258 | 136 | 157 | 192 | 176 |
| | | 220 | 274 | 240 | 260 | 215 | 235 | 168 | 182 | 180 | 150 |
| 1,1,1-trichloroethane | 91.1 | 74.0 | 90.0 | 70.0 | 69.0 | 58.0 | 77.0 | 57.2 | 44.0 | 63.3 | 57.1 |
| | | 74.0 | 95.0 | 53.0 | 60.0 | 65.0 | 71.0 | 50.7 | 59.7 | 56.9 | 47.7 |
| 1,2-dichloroethane | 90.2 | 75.0 | 77.0 | 75.0 | 82.0 | 75.0 | 84.0 | 60.2 | 51.4 | 59.6 | 58.9 |
| | | 72.0 | 88.0 | 78.0 | 86.0 | 72.0 | 75.0 | 53.8 | 58.3 | 58.4 | 59.8 |
| trichloroethene | 213 | 181 | 187 | 182 | 195 | 193 | 201 | 157 | 121 | 178 | 138 |
| | | 162 | 213 | 184 | 200 | 197 | 176 | 131 | 143 | 143 | 113 |
| tetrachloroethene | 237 | 197 | 203 | 213 | 207 | 183 | 213 | 177 | 120 | 189 | 145 |
| | | 195 | 233 | 199 | 200 | 188 | 195 | 144 | 159 | 156 | 123 |

[a] Results for duplicate samples for each treatment.
[b] Duplicate sample not analyzed.
Trans:     sample transported.
Not trans: sample not transported.


## TABLE 3-8(b). SUMMARY OF TRANSPORT STUDY RESULTS FOR HIGH SPIKED SAMPLES

| | Mean Concentration | | Standard Deviation | | %RSD | | Mean %R | | Diff. in Mean %R |
| Compound | Trans | Not Trans | Trans | Not Trans | Trans | Not Trans | Trans | Not Trans | |
|---|---|---|---|---|---|---|---|---|---|
| vinyl chloride | 303.9 | 300.5 | 43.6 | 32.0 | 14.3 | 10.6 | 135.6 | 132.4 | -1.5 |
| 1,1-dichloroethene | 47.6 | 47.9 | 4.9 | 6.6 | 10.3 | 13.7 | 104.4 | 105.1 | 0.7 |
| trans-1,2-dichloroethene | 109.4 | 110.6 | 12.2 | 20.3 | 11.2 | 18.4 | 79.3 | 80.2 | 0.9 |
| 1,1-dichloroethane | 69.5 | 70.6 | 7.2 | 12.4 | 10.3 | 17.5 | 76.3 | 77.5 | 1.2 |
| cis-1,2-dichloroethene | 203.5 | 217.9 | 33.9 | 46.6 | 16.7 | 21.4 | 72.4 | 77.5 | 5.1 |
| 1,1,1-trichloroethane | 62.2 | 67.0 | 8.4 | 16.8 | 13.5 | 25.1 | 68.3 | 73.5 | 5.2 |
| 1,2-dichloroethane | 67.9 | 72.0 | 8.8 | 13.6 | 13.0 | 18.9 | 75.3 | 79.9 | 4.6 |
| trichloroethene | 170.8 | 168.7 | 21.8 | 36.6 | 12.7 | 21.7 | 80.2 | 79.2 | -1.0 |
| tetrachloroethene | 184.1 | 179.8 | 20.6 | 39.9 | 11.2 | 22.2 | 77.7 | 75.9 | -1.8 |

Mean Concentration:     Mean concentration for duplicate samples for five sample pairs.
%RSD:     Prcent relative standard deviation.
Mean %R:     Mean percent recovery for duplicate samples for five sample pairs.
Difference in mean %R:  Difference in mean percent recovery between samples not transported and those transported.

concentrations; however, responses for TCE and PCE show some nonlinearity in the superhigh-concentration range. The elevated concentrations of those compounds (in the TT, as well as in the superhigh-concentration SPEW samples) required use of the smallest sampling loop. One explanation for this finding could be carryover of those compounds in that loop.

## Quality Assurance and Quality Control Results

### Results for QC Samples

#### QCCS Results: Percent Recoveries

Measured concentrations for the QCCS samples are shown in Tables 3-9(a,b). Percent recovery results are presented in Tables 3-10(a,b). Figure 3-4 shows QCCS %R results for each compound for both the AVOAS and EMSL-LV.

*Method 502.2* — With the exception of 1,1-DCE, all but two (of 30) data points for the EMSL-LV QCCS samples were within the DQO of 100 ±30 %R. The theoretical spike value for 1,1-DCE was 2.0 µg/L; five of the six %Rs for 1,1-DCE were between 175 and 195%, or 3 to 4 µg/L. The impact of the 1,1-DCE results in this demonstration was minimal. Two other results exceeded the DQO: one for VC and one for 1,1,1-TCA.

*AVOAS* — AVOAS results for VC were more variable than those of EMSL-LV, with %Rs ranging from 64-170%. Four of the six recoveries for VC exceeded ±30 %R of the theoretical spiked concentration. In contrast to the EMSL-LV results, only one 1,1-DCE result exceeded ±30% of the target value. TCE, PCE, and 1,1,1-TCA each had one value that exceeded ±30% of the target value.

For both EMSL-LV and the AVOAS, all compounds (except 1,1,1-TCA for EMSL-LV) had their highest %R on the first day of analysis. For

**TABLE 3-9(a). QUALITY CONTROL CHECK STANDARD RESULTS FOR EMSL-LV**

| Compound | Target Conc. (µg/L) | Detected Concentration, µg/L, by Day | | | | | | Summary | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | Mean Conc. (µg/L) | Standard Deviation | %RSD |
|---|---|---|---|---|---|---|---|---|---|---|
| vinyl chloride | 20.0 | 27.2 | 22.6 | 23.9 | 25.0 | 25.3 | 21.4 | 24.2 | 2.1 | 8.5 |
| 1,1-dichloroethene | 2.0 | 3.9 | 3.6 | 3.9 | 3.6 | 3.5 | 2.4 | 3.5 | 0.6 | 16.0 |
| 1,1,1-trichloroethane | 10.0 | 10.0 | 7.9 | 9.0 | 10.1 | 8.4 | 6.5 | 8.7 | 1.4 | 15.8 |
| trichloroethene | 2.0 | 1.9 | 1.6 | 1.8 | 1.8 | 1.6 | 1.8 | 1.8 | 0.1 | 7.0 |
| tetrachloroethene | 15.0 | 16.7 | 13.7 | 15.1 | 14.8 | 13.7 | 14.0 | 14.7 | 1.2 | 7.9 |

**TABLE 3-9(b). QUALITY CONTROL CHECK STANDARD RESULTS FOR THE AVOAS**

| Compound | Target Conc. (µg/L) | Detected Concentration, µg/L, by Day | | | | | | Summary | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | Mean Conc. (µg/L) | Standard Deviation | %RSD |
|---|---|---|---|---|---|---|---|---|---|---|
| vinyl chloride | 20.0 | 33.9 | 29.8 | 12.8 | 15.9 | 25.6 | 27.7 | 24.3 | 8.2 | 33.8 |
| 1,1-dichloroethene | 2.0 | 2.3 | 1.7 | 1.1 | 1.4 | 1.7 | 1.9 | 1.7 | 0.4 | 24.4 |
| 1,1,1-trichloroethane | 10.0 | 15.2 | 11.4 | 8.0 | 7.2 | 9.2 | 10.8 | 10.3 | 2.9 | 28.1 |
| trichloroethene | 2.0 | 5.4 | 2.1 | 1.4 | 1.4 | 1.9 | 2.3 | 2.4 | 1.5 | 61.9 |
| tetrachloroethene | 15.0 | 18.3 | 13.9 | 9.6 | 10.9 | 11.9 | 14.1 | 13.1 | 3.1 | 23.3 |

%RSD:    Percent relative standard deviation
Mean % R:    Mean percent recovery.

the following days, results for 1,1,1-TCA, TCE, and PCE tended to be near or less than 100% R. The cause for either of these observations is uncertain.

## QCCS Results: Precision

*Method 502.2* — Percent RSDs for EMSL-LV analyses ranged from 7 to 16% among compounds.

*AVOAS* — For the AVOAS QCCS samples, although the mean %Rs for each compound across days were good (84 to 122%), the %RSDs tended to be high, ranging from 23 to 62%. The 62 %RSD for TCE is a result of an inexplicably high %R of approximately 270% on the first day of analysis.

The variability for the EMSL-LV QCCS samples was notably less than that for the AVOAS, probably because the QCCS used by EMSL-LV was prepared from a single ampoule spiked into reagent water, and the same solution was used for the entire demonstration; for the QCCS used for the AVOAS. A new ampoule was opened daily and

a fresh standard was prepared. As one would expect, this procedure led to less variability in the EMSL-LV results than those of the AVOAS for the QCCS analyses. Variabilities in spiking technique and in analyte concentrations in the commercially prepared spiking solutions would be expected to contribute to the lower precision values for the AVOAS.

## Surrogate Recoveries

A surrogate compound was not used for the AVOAS analyses. Surrogate (2-bromo-1-chloropropane) recoveries ranged from 85 to 116%, all within the 80 to 120% acceptance limits for Method 502.2.

## Instrument Blank Results

*Method 502.2* — Instrument blanks showed no analytes present at concentrations greater than the MDLs.

*AVOAS* — The blank samples run on the AVOAS showed small amounts of one or more of

## TABLE 3-10(a). PERCENT RECOVERIES FOR QUALITY CONTROL CHECK STANDARDS FOR EMSL-LV

| Compound | Percent Recovery, by Day | | | | | | Summary | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | Mean % R | Standard Deviation | %RSD |
|---|---|---|---|---|---|---|---|---|---|
| vinyl chloride | 136 | 113 | 120 | 125 | 127 | 107 | 121 | 10.4 | 8.6 |
| 1,1-dichloroethene | 195 | 180 | 195 | 180 | 175 | 120 | 174 | 27.8 | 16.0 |
| 1,1,1-trichloroethane | 100 | 79.0 | 90.0 | 101 | 84.0 | 65.0 | 86.5 | 13.6 | 15.8 |
| trichloroethene | 95 | 80.0 | 90.0 | 90.0 | 80.0 | 90.0 | 87.5 | 6.1 | 7.0 |
| tetrachloroethene | 111 | 91.3 | 101 | 98.7 | 91.3 | 93.3 | 97.8 | 7.6 | 7.8 |

## TABLE 3-10(b). PERCENT RECOVERIES FOR QUALITY CONTROL CHECK STANDARDS FOR THE AVOAS

| Compound | Percent Recovery, by Day | | | | | | Summary | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | Mean %R | Standard Deviation | %RSD |
|---|---|---|---|---|---|---|---|---|---|
| vinyl chloride | 170 | 149 | 64.0 | 79.5 | 128 | 139 | 122 | 41.3 | 33.9 |
| 1,1-dichloroethene | 115 | 85.0 | 55.0 | 70.0 | 85.0 | 95.0 | 84.2 | 20.6 | 24.5 |
| 1,1,1-trichloroethane | 152 | 114 | 80.0 | 72.0 | 92.0 | 108 | 103 | 28.8 | 28.0 |
| trichloroethene | 270 | 105 | 70.0 | 70.0 | 95.0 | 115 | 121 | 75.3 | 62.3 |
| tetrachloroethene | 122 | 92.7 | 64.0 | 72.7 | 79.3 | 94.0 | 87.5 | 20.5 | 23.4 |

the target analytes; however, with the exception of PCE, all were at concentrations less than the MDL or PQL of the instrument. The PQL for the 10-mL sampling loop used for blanks was 0.10 µg/L for PCE; PCE was present in all blanks at approximately 0.3 to 1.2 µg/L. However, because the lowest sample concentration of PCE in this study was 15 µg/L (in the QCCS), no data were invalidated by the presence of the small amounts of PCE detected in the blanks.

## Travel Blank Results

Travel blank samples were not run for the AVOAS, because samples were not shipped.
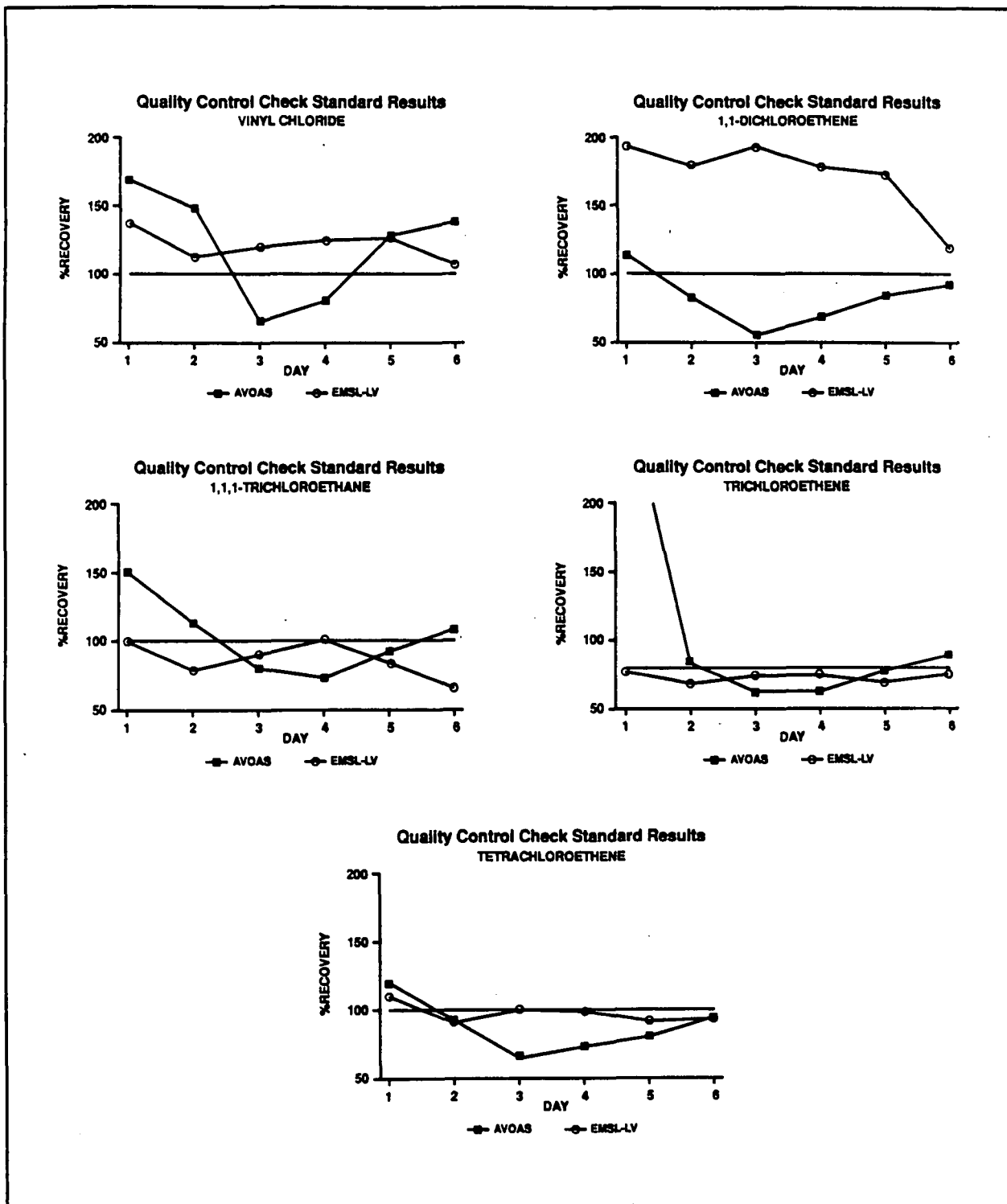


**Figure 3-4. Quality Control Check Standard Results.**

Travel blanks analyzed by EMSL-LV during the demonstration contained concentrations of PCE below the MDL; 1,1,1-TCA was detected in one blank at a concentration less than the PQL. Thus, no demonstration data were impacted by contamination during transport.

## Continuing Calibration Check Standard Results

Continuing calibration check standard results for EMSL-LV and the AVOAS are shown in Tables 3-11(a,b).

**TABLE 3-11(a). PERCENT DIFFERENCES FOR CONTINUING CALIBRATION CHECK STANDARDS FOR EMSL-LV**

| Compound | Percent Difference, by Day | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| vinyl chloride | 6.4 | 0.7 | 5.8 | 6.8 | 3.9 | 0.85 |
| 1,1-dichloroethene | -5.6 | 2.3 | 6.4 | 5.4 | 4.5 | 0.30 |
| trans-1,2-dichloroethene | -7.9 | 2.6 | 4.4 | 2.7 | 1.4 | -7.1 |
| 1,1-dichloroethane | -8.2 | 1.0 | 4.8 | 2.4 | 1.3 | -6.2 |
| cis-1,2-dichloroethene | -9.6 | 2.7 | 4.9 | 7.2 | 1.3 | -2.6 |
| 1,1,1-trichloroethane | -14.8 | -7.1 | -5.6 | -5.3 | -10.0 | -12.7 |
| 1,2-dichloroethane | -8.3 | 2.0 | 4.3 | 6.8 | 0.6 | -2.2 |
| trichloroethene | -10.6 | 1.1 | 1.1 | 4.0 | -0.7 | -3.8 |
| tetrachloroethene | -14.4 | 3.2 | 3.2 | 4.3 | -0.2 | -6.3 |

**TABLE 3-11(b). PERCENT DIFFERENCES FOR CONTINUING CALIBRATION CHECK STANDARDS FOR THE AVOAS**

| Compound | Percent Difference, by Day | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| vinyl chloride | -8.3 | 28.4 | -10.7 | 35.5 | 30.5 | 24.9 |
| 1,1-dichloroethene | 2.3 | 16.3 | 9.9 | 21.6 | 24.9 | 21.2 |
| trans-1,2-dichloroethene | -6.4 | -0.18 | -9.3 | 3.1 | -1.2 | -6.8 |
| 1,1-dichloroethane | -8.6 | -5.6 | -9.1 | -4.0 | -7.8 | -13.2 |
| cis-1,2-dichloroethene | -7.0 | -3.3 | -6.2 | -2.0 | -5.5 | -11.8 |
| 1,1,1-trichloroethane | -20.1 | -13.6 | -22.9 | -7.4 | -18.8 | -30.1 |
| 1,2-dichloroethane | -3.6 | 1.7 | 1.9 | -1.5 | -2.9 | -9.5 |
| trichloroethene | -10.2 | -5.9 | -10.8 | -6.2 | -9.9 | -16.4 |
| tetrachloroethene | -7.5 | -4.0 | -8.3 | -5.8 | -6.8 | -18.6 |

Percent Difference = $C_1$-$C_2$ • 100/$C_1$; $C_1$ = response for initial calibration; $C_2$ = response for continuing calibration.
EMSL-LV data are the mean of two measurements.
Target concentrations for all analytes for EMSL-LV were 20 µg/L, and for the AVOAS, 400 µg/L.

*Method 502.2* — All %Ds for the EMSL-LV CCCSs were within the acceptance criteria of <20 %D. The EMSL-LV instrument was recalibrated once, on the second day of the demonstration because %Ds of nearly 15% were noted for two compounds on the first day. All EMSL-LV samples were analyzed within acceptable instrument calibration.

*AVOAS* — Over the 6 days of analysis, 10 of 54 of the %Ds for individual analytes were >20%. These high %Ds occurred with three compounds: VC, 1,1-DCE, and 1,1,1-TCA. Two of the VC responses exceeded 30 %D. If the data associated with those two CCCSs are considered suspect, 10 of the 30 spiked sample results would be invalid. Most of these are for VC, for which the majority of QCCS and SPEW samples had %Rs in excess of 100 ±30%.

### Results for Data Quality Objectives

### Representativeness

To determine whether or not the data from spiked samples introduced into the AVOAS in the off-line mode were representative of data obtained when the instrument was operated in the automated mode, the results for AVOAS on-line and off-line TT samples were compared. Vinyl chloride and 1,2-DCA were not detected by the AVOAS or EMSL-LV in the TT samples. Of the remaining seven analytes, the difference between the on-line and off-line AVOAS results was not significant or only slightly significant for most compounds. The TT sample results indicate that data generated using off-line spiked samples should be representative of data generated by the AVOAS in an on-line, automated mode.

### Completeness

The QC data for the EMSL-LV instrument indicated acceptable conditions for all measurements. For the AVOAS, although data in excess of the QC limits occurred, no statistical outliers were identified. All of the AVOAS data values were utilized in performing the statistical tests and in developing the conclusions for this demonstration. Completeness is therefore considered to be 100%.

### Accuracy

Comparisons of accuracy results for the AVOAS and EMSL-LV were made using %R data for QCCS and SPEW samples. The QCCS data

were discussed previously and are summarized in Table 3-10(a,b).

SPEW sample differences in mean %R results were discussed previously. Percent recoveries for individual days are presented in Tables 3-12(a,b). A total of 210 %Rs for SPEW samples were collected on each of the instruments.

*Method 502.2* — Percent recoveries ranged from 48 to 122%, with no results above the limit and 39% of the results below 70 %R.

*AVOAS* — Fourteen percent of the AVOAS SPEW sample results were in excess of ±30% of the target concentrations; recoveries for those samples were all greater than 100%. Only three of the 24 VC recoveries were within 100 ±30 %R. Analytes other than VC with %Rs that exceeded 100 ±30% included 1,2-DCA, 1,1,1-TCA, TCE, and PCE. With the exception of VC, virtually all of the analyte results were within a 100 ±50 %R window.

### Precision

Precision for TT and SPEW sample results was discussed earlier. Precision for AVOAS and EMSL-LV QCCS sample results are not comparable because of the different QCCS preparation procedures used.

### Comparability

Results concerning the comparability of the AVOAS and Method 502.2 were discussed previously in the sections on TT, SPEW, and QCCS sample results.

### Performance and Systems Audits

Performance audits use samples spiked with known concentrations of analytes to quantitatively evaluate the measurement capability of a system. No samples were specifically designated as performance audits in this demonstration, because many of the samples were inherently similar to performance audit samples. That is, they were samples spiked with known concentrations of target analytes.

Systems audits are qualitative evaluations of operational details, performed to ensure that the protocols of the QAPjP are properly implemented. Systems audits were conducted at both the EMSL-LV laboratory and the Woburn site early in the demonstration by experienced QA auditors from LESC. Facilities, equipment, and operations (such as sample collection and handling, record-

keeping, chain-of-custody and sample tracking, data reporting, and QA procedures) were audited. The EMSL-LV audit indicated satisfactory conditions and compliance with the QAPjP. For the field site, no serious problems were found. The absence of written operating procedures for the AVOAS was noted. Also, high variability in the early QCCS results for the AVOAS was observed; however, it was too early in the study to determine the significance of or to identify a cause for that finding.

## Qualitative Observations

The short duration of this demonstration did not permit a comprehensive qualitative evaluation

of the AVOAS. However, several observations regarding system features were made incidental to the field demonstration and these are summarized below.

## Ruggedness and Adaptability

The AVOAS hardware is well-designed and ruggedly constructed. The system is sturdy and without extraneous frills or packaging. The basic components are visible and accessible, facilitating maintenance and troubleshooting. The AVOAS components are designed to accommodate field-automated analyses: the stripping cell is self-cleaning between sampling events; sample port and sample volume can be automatically or manu-

**TABLE 3-12(a). PERCENT RECOVERIES FOR SPIKED PURGED EFFLUENT WATER SAMPLES FOR EACH DEMONSTRATION DAY FOR EMSLV**

| Compound | Low Spike | | | | | | Medium Spike | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 | 6 |
| vinyl chloride | 92.9 | 89.7 | 47.8 | 92.0 | 96.4 | 90.2 | 104.0 | 78.9 | 70.1 | 74.9 | 90.6 | 72.2 |
| 1,1-dichloroethene | 87.7 | 87.7 | 61.4 | 85.5 | 92.1 | 109.6 | 73.5 | 60.4 | 58.2 | 53.7 | 63.7 | 48.6 |
| trans-1,2-dichloroethene | 71.9 | 71.9 | 53.8 | 71.2 | 74.9 | 71.2 | 77.9 | 67.7 | 63.6 | 58.5 | 62.6 | 53.3 |
| 1,1-dichloroethane | 71.4 | 73.5 | 56.0 | 71.4 | 76.8 | 73.5 | 86.4 | 83.8 | 78.9 | 72.1 | 75.7 | 64.5 |
| cis-1,2-dichloroethene | 76.6 | 76.6 | 61.3 | 74.5 | 81.6 | 74.5 | 86.5 | 81.0 | 75.5 | 68.4 | 70.5 | 59.9 |
| 1,1,1-trichloroethane | 61.5 | 71.4 | 56.0 | 67.0 | 77.9 | 122.9 | 81.2 | 73.5 | 68.1 | 63.7 | 68.1 | 65.9 |
| 1,2-dichloroethane | 78.7 | 76.5 | 67.6 | 75.4 | 86.5 | 74.3 | 84.4 | 85.7 | 82.1 | 73.7 | 71.7 | 68.6 |
| trichloroethene | 76.5 | 78.3 | 61.9 | 75.0 | 86.3 | 75.5 | 75.3 | 75.5 | 71.0 | 64.3 | 65.6 | 55.8 |
| tetrachloroethene | 80.2 | 81.6 | 64.6 | 76.0 | 87.8 | 83.2 | 84.6 | 74.4 | 71.0 | 62.0 | 63.1 | 52.7 |

| Compound | High Spike | | | | | | Super High Spike | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 | 6 |
| vinyl chloride | 107.0 | 79.2 | 76.2 | 104.0 | 120.7 | 102.2 | 77.6 | 68.3 | 77.6 | 60.2 | 97.7 | 84.3 |
| 1,1-dichloroethene | 92.1 | 66.2 | 71.7 | 88.2 | 103.5 | 84.9 | a | a | a | a | a | a |
| trans-1,2-dichloroethene | 76.3 | 57.4 | 59.6 | 74.1 | 90.1 | 69.8 | 68.3 | 63.7 | 60.1 | 49.8 | 68.9 | 62.2 |
| 1,2-dichloroethane | 74.6 | 59.3 | 60.4 | 75.7 | 88.9 | 68.1 | 79.0 | 74.6 | 68.1 | 59.3 | 76.8 | 79.0 |
| cis-1,2-dichloroethene | 79.5 | 60.2 | 62.0 | 76.3 | 87.3 | 68.4 | 73.9 | 65.3 | 61.2 | 55.9 | 65.5 | 70.4 |
| 1,1,1-trichloroethane | 67.0 | 68.1 | 58.2 | 71.4 | 94.4 | 75.7 | 70.3 | 69.7 | 71.9 | 59.3 | 75.7 | 70.3 |
| 1,2-dichloroethane | 80.9 | 66.5 | 63.2 | 79.8 | 87.6 | 73.2 | 82.5 | 73.6 | 67.3 | 62.6 | 72.3 | 69.8 |
| trichloroethene | 80.7 | 66.6 | 63.8 | 74.6 | 87.7 | 69.9 | 75.9 | 68.4 | 64.7 | 55.3 | 70.3 | 67.5 |
| tetrachloroethene | 83.6 | 66.7 | 64.6 | 76.0 | 86.1 | 68.4 | 82.3 | 69.9 | 78.4 | 57.5 | 73.8 | 67.6 |

a 1,1-dichloroethene was not spiked into superhigh-concentration spiked purged effluent water samples.

ally selected; and the system can be adapted to different purgeable analytes by using the appropriate GC column, temperature program, and detector.

### Maintenance Requirements

The maintenance requirements of this instrument are similar to those for other analytical instrumentation. Routine GC maintenance procedures are required, e.g., changing gas cylinders, cleaning detectors, and replenishing integrator paper. System-specific maintenance includes cleaning or changing the inlet water filters to the injector (about once a day); changing the peristaltic pump tubes on the injector (about once a week); and changing the drying trap on the injector (about once a week). These routine maintenance procedures do not appear to be time-consuming or difficult.

According to the AVOAS developer, they can be completed in less than 15 min and can be done at the time of the continuing calibration check.

### Facility and Supplies Requirements

The AVOAS requires an environment consistent with that found in an analytical laboratory: a sturdy bench or tabletop (approximately 80 x 30 in), a clean source of water, constant temperature (ideally 20°C, ± 3°C), and a relatively clean, VOC-free environment. If telecommunications are desired, a dedicated telephone line is necessary. The instrument is not suitable for quick setup in a harsh environment (e.g., as required for emer-

**TABLE 3-12(b). PERCENT RECOVERIES FOR SPIKED PURGED EFFLUENT WATER SAMPLES FOR EACH DEMONSTRATION DAY FOR THE AVOAS**

| Compound | Low Spike | | | | | | Medium Spike | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 | 6 |
| vinyl chloride | 145.7 | 164.3 | 125.1 | 135.4 | 141.1 | 142.9 | 160.9 | 151.3 | 138.4 | 92.8 | 145.7 | 155.0 |
| 1,1-dichloroethene | 97.8 | 98.0 | 82.5 | 94.5 | 91.9 | 98.2 | 82.3 | 79.0 | 74.5 | 47.4 | 78.0 | 76.8 |
| trans-1,2-dichloroethene | 96.3 | 99.1 | 86.9 | 74.1 | 78.4 | 99.0 | 100.6 | 102.1 | 93.2 | 62.1 | 72.9 | 99.6 |
| 1,1-dichloroethane | 101.3 | 104.5 | 95.5 | 95.1 | 103.7 | 106.7 | 122.4 | 117.6 | 114.5 | 75.4 | 117.0 | 120.4 |
| cis-1,2-dichloroethene | 96.5 | 101.3 | 93.9 | 97.9 | 106.7 | 97.3 | 107.4 | 105.7 | 97.7 | 63.8 | 99.2 | 100.8 |
| 1,1,1-trichloroethane | 95.9 | 104.1 | 93.9 | 104.5 | 114.4 | 189.5 | 120.6 | 118.0 | 114.0 | 69.1 | 106.9 | 123.1 |
| 1,2-dichloroethane | 97.6 | 97.1 | 93.4 | 98.8 | 106.2 | 102.5 | 116.0 | 108.2 | 102.0 | 71.5 | 111.3 | 108.6 |
| trichloroethene | 96.0 | 104.0 | 92.1 | 93.4 | 100.8 | 105.6 | 104.9 | 106.3 | 94.9 | 63.4 | 96.5 | 103.4 |
| tetrachloroethene | 92.0 | 98.4 | 88.9 | 90.7 | 93.2 | 104.7 | 99.9 | 101.2 | 92.8 | 58.9 | 90.4 | 102.9 |

| Compound | High Spike | | | | | | Superhigh Spike | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 | 6 |
| vinyl chloride | 146.1 | 157.0 | 118.3 | 130.7 | 132.5 | 136.7 | 162.1 | 138.9 | 151.4 | 124.5 | 163.1 | 189.4 |
| 1,1-dichloroethene | 97.7 | 101.1 | 87.3 | 89.7 | 103.0 | 103.7 | a | a | a | a | a | a |
| trans-1,2-dichloroethene | 95.7 | 97.8 | 85.8 | 82.8 | 74.6 | 98.1 | 104.0 | 100.4 | 93.7 | 90.1 | 97.5 | 108.6 |
| 1,1-dichloroethane | 98.7 | 98.5 | 91.8 | 88.5 | 102.6 | 98.9 | 121.7 | 106.4 | 104.1 | 96.7 | 103.7 | 121.9 |
| cis-1,2-dichloroethene | 95.0 | 96.3 | 88.3 | 77.3 | 101.6 | 94.4 | 117.1 | 104.7 | 97.5 | 92.0 | 99.1 | 114.5 |
| 1,1,1-trichloroethane | 94.4 | 96.0 | 89.5 | 75.8 | 110.3 | 97.8 | 130.0 | 102.1 | 106.8 | 92.0 | 108.3 | 136.9 |
| 1,2-dichloroethane | 95.4 | 91.6 | 88.2 | 76.4 | 102.9 | 99.0 | 114.0 | 99.5 | 100.0 | 87.1 | 94.8 | 121.2 |
| trichloroethene | 97.3 | 102.0 | 93.0 | 80.2 | 103.2 | 104.2 | 119.7 | 114.3 | 105.6 | 100.4 | 105.1 | 124.1 |
| tetrachloroethene | 96.3 | 98.2 | 91.2 | 79.7 | 98.9 | 105.7 | 125.5 | 120.0 | 108.7 | 110.4 | 109.1 | 138.1 |

[a] 1,1-dichloroethene not spiked into superhigh-concentration spiked purged effluent water samples.

gency-response screening analyses), but is designed for long-term monitoring in an undisturbed location. A constant 20-A, 120-V power source is required. Any extended interruptions in power require a warmup time to ensure that the detection system has reached a stable equilibrium. After a power interruption, a calibration check is required to ensure that the system instrument has not changed.

A water supply is required for flushing the lines and sample loops between analyses. The AVOAS includes a sparging system that uses high-purity inert gas to purge a water source of VOCs. At most sites, local tapwater could be used as a source for rinse-water. Otherwise, bottled purified water can be used.

The instrument should be operated in a constant-temperature environment because a fluctuation of more than a few degrees would probably alter the sparging efficiencies of the target volatile analytes. This situation was not encountered or studied during the demonstration.

Provision must be made for treatment and disposal of waste water generated by the AVOAS during its operation. Several liters of treatment train water (500 mL/min for several minutes) are generated during sampling. The amount depends on the length of the sampling lines. At the Woburn site, the contaminated waste water was collected and recycled into the treatment system, so waste water disposal was not a problem.

In addition to compressed gases used to operate the GC, the AVOAS requires zero-grade helium for the injector purge gas, and standard-grade helium for the rinse-water purification system. Other supplies are the same as those required for standard GC analyses of VOCs in water.

### System Costs

The AVOAS is currently not for sale. The developer intends to initially lease AVOAS units at rates that will depend upon the specific system configuration; a one-time fee for system setup and operator training will be charged. An additional expense in using the AVOAS would be that for an operator. Although an operator was present for about 14 hr/day during the demonstration, during routine monitoring, an operator's presence would be required for at most 1 hr/day.

The AVOAS was leased at the Wells G and H Superfund Site for $8000 per month. Assuming that 20 samples/day could be processed under rou-

tine monitoring operations (not including QC samples), the cost per sample over a month would be less than $15, not including operator labor cost. The cost per sample for comparable analysis by conventional methods is approximately $225-275, depending on the method used and the number of target analytes. However, because of sample turnaround time (usually on the order of several days), conventional methods are not typically suited to high-frequency, long-term monitoring, so the costs may not be directly comparable.

### Summary of Results and Discussion

1. For most of the TT samples, concentrations measured by the AVOAS in the on-line mode were slightly higher than those measured off-line; however, the difference was not significant for most compounds. This indicated that the findings for samples analyzed off-line (e.g., SPEW and QCCS samples) could be considered representative of on-line performance, and could be used for comparisons of the AVOAS and EMSL-LV results.

2. Nearly all recoveries for both TT and SPEW samples were higher for the AVOAS than for the EMSL-LV analyses. However, the overall mean %R for EMSL-LV (for all compounds, concentration ranges, and days) for SPEW samples was 74%, in comparison to 104% for the AVOAS. These findings seem to indicate that the AVOAS gave results more nearly equivalent to the target concentrations than EMSL-LV. QCCS %R results for EMSL-LV close to 100% and CCCS results consistently within acceptable ranges would seem to argue against a problem in instrument calibration. Transport or holding time effects are a possible explanation for the finding of lower EMSL-LV analyte concentrations.

3. The effect of transport on sample results is open to question. The variability due to analyst appears to exceed that due to transport.

4. Treatment train samples analyzed by the AVOAS in the afternoon had slightly higher analyte concentrations than those analyzed in the morning, especially for the less volatile compounds. This finding is consistent with carryover from superhigh-concentration SPEW samples analyzed between the morning and the afternoon. Both TT and superhigh-SPEW samples were collected through the smallest sampling loop. The increases in concentration are, however, low enough to be of no practical significance.

5. AVOAS %R results for vinyl chloride were variable and substantially exceeded those for other compounds analyzed by that system, and they were proportionately higher than those of the EMSL-LV analyses. The source of the problem cannot be determined from the demonstration data. If the AVOAS were considered for use at a site having vinyl chloride as a contaminant, the system's performance in measuring that compound would need to be more rigorously evaluated.

The question of false-positive results arises with respect to compounds detected by the AVOAS but not by EMSL-LV in the TT samples. In all of the sample pairs for which the AVOAS had detectable concentrations of compounds but EMSL-LV did not, the concentrations measured by the AVOAS were less than the detection limits for the EMSL-LV instrument. Thus, it is unlikely that the AVOAS results reflect false positives.

Although false-negative results (i.e., not detecting a contaminant when in fact it is present) were not studied in this evaluation, such erroneous results are possible, and steps should be taken to minimize them. The consequence of a false-negative result could be to not recognize a failure or decline in function of some component in the treatment system. False-negative results could potentially occur if there were a problem in either the sampling or the analytical system; for example, if a sampling line were clogged or if the manifold were not functioning properly. Ongoing instrument calibration checks are important, as are confirmatory analyses, particularly of samples from effluent ports, where the risk of actual VOC concentrations exceeding measured values is of most concern; i.e., where the potential exists for releasing water containing VOC concentrations above the allowable effluent limits.

The data from this study were also evaluated by Stanley Deming and John Palasota, of the University of Houston Department of Chemistry under a cooperative agreement with the EMSL-LV. Their findings are summarized in a technical report submitted to the EPA through a cooperative agreement. Although their approach to data analysis was somewhat different (i.e., ratios of paired data rather than differences in mean %Rs were evaluated), the findings were similar. That is, the AVOAS gave results that were comparable to those obtained using Method 502.2. Bias exists; the AVOAS results are high compared to the EMSL-LV results. The source for this bias is not possible to determine from the data of this study. Possible explanations could include calibration differences between the two locations or degradation of samples due to sample shipment and holding time. The QC data do not indicate a calibration problem, and the potential for a holding time effect is not supported by the TT sample data or the transport study results. Whether bias would occur in general (i.e., for routine use of the AVOAS) is yet to be learned.

An interpretation of the data from this demonstration, and any extension of the results to other similar evaluations, must be tempered by several considerations. Throughout the demonstration the AVOAS was being operated by its inventor, who was there daily monitoring and adjusting its performance. Also, the demonstration was conducted shortly after the system was installed, so that any long-term effects, such as loss in performance due to wear and tear on the system or contamination of its various components (e.g., sampling lines, manifold, sampling loops, sparging unit) could not be evaluated.

# Section 4
## Conclusions and Recommendations

## Conclusions

The AVOAS demonstration went smoothly, and was considered by both the AVOAS developer and EMSL-LV to be a fair evaluation of its performance under the study conditions. All samples specified by the demonstration design were analyzed, and all of the data were judged to be of sufficient quality to be included in the data base upon which the following conclusions for this demonstration are made. The qualitative and quantitative findings generated in this demonstration provided the basis for the following conclusions regarding the performance of the AVOAS:

1. Mean concentration values generated by the AVOAS for all analytes in all SPEW and TT treatment train samples were higher than those measured by Method 502.2. The cause of this bias is difficult to determine from the data available. The bias is more likely due to sample holding time and/or transportation effects, analyst techniques for calibration, preparing spiked samples, or analysis, or some combination of these, than to the instrument itself.

2. The precision obtained by the AVOAS was comparable to that obtained by the laboratory instrument, within the range of expected variability for samples containing VOCs.

3. The AVOAS performed well in analyzing samples with VOC concentrations in the low-ppb to ppm range.

4. The system used by the AVOAS for stripping VOCs from water (one of the proprietary features of the AVOAS) is simple in design and function, self-cleaning, and more adaptable to field automation than the traditional purge-and-trap procedure.

5. The fact that the AVOAS was operational shortly after installation, and was running nearly 24 hours per day for the duration of this demon-

stration indicates the potential reliability of the system is high.

6. Based on the findings of this demonstration, the AVOAS appears to have the potential to provide data comparable to that which would be obtained using established sampling and analytical methods. The discrepancies in accuracy and precision are not substantial enough to offset the advantages of the system and are probably attributable factors other than instrument performance.

## Advantages of the AVOAS

1. The AVOAS is simple in design, and has easily accessible components. The LESC scientist present at the field site observed that the minor instrumental problems encountered during the 6 days of analysis were relatively easy to diagnose and repair.

2. The AVOAS appears to be capable of providing the benefits of automated sampling and analysis discussed in Section 1 of this report; i.e., rapid results and the elimination of separate sample collection, handling, shipping, and analysis steps.

3. The potential cost savings per sample for use of the AVOAS in comparison to use of established methods could be substantial. Savings would be realized not only in the activities related to sampling and analysis, but in the increased efficiency brought about by real-time monitoring of the performance of ground-water treatment systems. We must emphasize that, with a dedicated, on-line system, sampling frequency would probably be greater than if conventional methods were used. For that reason, the cost per sample would be lower. In addition, the likelihood of detecting a change in system performance would be increased.

## Limitations of the AVOAS

Although the following items were identified as potential limitations to the AVOAS, many of them are merely factors to be kept in mind by prospective users of the AVOAS. The AVOAS developer has since taken steps to correct equipment or procedural problems.

1. The AVOAS requires a temperature-controlled environment in an atmosphere free of contamination. Extra measures to ensure these conditions may be required in a typical field situation or industrial facility.

2. Water samples high in particulate matter tend to clog a filter in the injector inlet. This problem can be minimized if water is pre-filtered before being conveyed to the AVOAS or if the inlet filters are cleaned or changed as part of the routine daily maintenance.

3. Internal standards cannot be analyzed by the AVOAS in the on-line mode. Such standards provide an ongoing indication of instrument performance. It is possible to indirectly monitor instrument performance through calibration checks and observation of analyte concentrations for each port. However, this approach is not recommended, and is not diagnostic for problems with the analytical versus the sampling and sparging portions of the system.

4. Carryover in the smallest sample loop of the AVOAS was suggested by the finding of an increase in trace concentrations of several analytes in TT samples between the morning and afternoon analyses. The corresponding EMSL-LV data do not reflect these findings. Because of the low concentrations involved, the possibility of carryover is not a serious impediment to use of the AVOAS for higher concentration analytes. The AVOAS developer has modified the design of the manifold to reduce dead volume significantly, and expects this change to greatly reduce the carryover problem.

5. The volume of sample injected by the smallest sampling loop was difficult to measure accurately because the dead volume of the sample valve (i.e., the internal volume of valve parts, aside from sample volume measurement hardware) was disproportionately large. The developer is examining better approaches to estimating volumes for each of the sampling loops.

6. Most of the problems, albeit minor, encountered with the AVOAS during the field demonstration were due to problems in the software. Some were solved during the demonstration, and plans were made to correct the others shortly after the demonstration was completed.

## Limitations of the AVOAS Demonstration

This demonstration was designed to evaluate specific aspects of the AVOAS performance relative to an established method; the demonstration was not a comprehensive evaluation of all of the proposed advantages or potential limitations of the system. The conditions of this demonstration were atypical of those that would probably exist under routine monitoring operations. A number of sample types were analyzed in the off-line mode and the demonstration was performed with the AVOAS inventor closely checking and adjusting the system's performance. The capability of the AVOAS to be operated unattended from a remote location under software control was not evaluated; nor were the repeatability and reliability of calibration and maintenance procedures, or the long-term performance of the system.

## Recommendations

Recommendations are made here specifically for the AVOAS and for future SITE Program demonstrations. A number of the issues encountered for the AVOAS demonstration design apply to the demonstration of virtually any technology. Resolution of these issues would facilitate collection of high quality data for future SITE demonstrations.

## Recommendations Specific to the AVOAS

1. Further development of the AVOAS is encouraged. A fair evaluation at a future stage of development would require monitoring the system's performance when operated totally in the automated mode, without interruption or intervention. Performance data should be generated for this system when used at other sites and by different operators.

2. Instrument calibration should be checked regularly, on a schedule based on the performance of the detector. A daily calibration check is recommended. If this is not feasible, at a minimum, detector performance should be monitored daily over a period of several weeks after instrument installation. An appropriate calibration schedule should be developed and followed for the long-

term use of the system, especially for unattended, remote operation.

3. A mechanism for introducing surrogate or internal standards into the AVOAS with each analysis would provide an ongoing indication of analytical instrument performance.

4. Depending on the data quality objectives for instrument performance at a particular site, blank samples should be periodically analyzed on all sampling loops used for analysis to ensure that carryover from high-concentration into low concentration samples is not occurring.

5. In this demonstration, response factors for three of the sampling loops were based on estimated loop sizes. Errors in estimating the sample loop sizes are thought to have influenced the calculated response factors for some of the loops, particularly the smallest size. A procedure for more accurately determining sample loop size should be developed. Alternatively, each sample loop should be individually calibrated.

6. During the initial stages of long-term monitoring, concentrations and precision for each sampling port should be closely monitored to generate baseline conditions. Also, periodic confirmatory analyses by established methods should be performed to verify AVOAS results.

7. An instruction and procedural manual for the system should be written. QA/QC procedures should be included as part of the standard operating procedures.

## Recommendations for Future Studies

1. A more rigorous evaluation of holding time and transport effects on measured concentrations of VOCs in water samples is recommended.

2. An investigation of the stripping efficiency for various VOCs from water, in purge and trap and similar processes (e.g., the method used by the AVOAS), for samples of different concentrations and volumes is recommended.

3. A study to distinguish the variability due to calibration-standard spiking procedures of various analysts from the variability due to instrument performance is recommended.

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